İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

CONTROLLED SYNTHESIS OF VINYL AMINE POLYMERS BY RAFT TECHNIQUE

M.Sc. Thesis by

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JUNE 2008

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TABLE OF CONTENTS

LIST of ABBREVIATIONS **v**
LIST of TABLES **vii**
LIST of FIGURES **viii**
LIST of SYMBOLS **ix**
SUMMARY **x**
ÖZET **xi**

1. INTRODUCTION **1**

2. THEORETICAL PART **3**
2.1. Block Copolymers 3
2.1.1. Applications of Block Copolymers 3
2.1.2. Amphiphilic Block Copolymers 4
2.1.2.1. Preparation of Nanoparticle Hybrids 6
2.1.2.2. Drug Delivery 7
2.1.2.3. Surfactant-based Applications 7
2.1.3. Synthesis of Linear AB Diblock Copolymers 8
2.1.3.1. Block Copolymers by Anionic Polymerization 8
2.1.3.2. Block Copolymers by Cationic Polymerization 9
2.1.3.3. Block Copolymers by Living Free Radical Polymerization 10
2.1.3.4. Block Copolymers by Group Transfer Polymerization 10
2.1.3.5. Block Copolymers by Ring Opening Metathesis Polymerization 12
2.1.3.6. Block Copolymers by Combination of Different Polymerization Methods 13
2.1.3.7. Block Copolymers by Chemical Modification 13
2.2. Controlled Living Radical Polymerization 14
2.2.1. Atom Transfer Radical Polymerization (ATRP) 16
2.2.2. Nitroxide Mediated Polymerization 17
2.2.3. Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) 18
2.3. Poly(vinylamine)s 22

3. EXPERIMENTAL WORK **25**
3.1. Materials and Chemicals 25
3.1.1. Monomers 25
3.1.2. Solvents 25

3.1.3. Other Chemicals 26
3.2. Equipment 27
3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR) 27
3.2.2 Gel Permeation Chromatography (G.P.C) 27
3.2.3 High Performance Liquid Chromatography (HPLC) 27
3.2.4 Fourier Transformation Infrared Spectrophotometer (FTIR) 27
3.2.5 Ubbelohde Viscometer 27
3.3. Synthethic Procedures 27
3.3.1. Preparation of RAFT Agent, Phenacyl Morpholinedithiocarbamate (PMD) 27
3.3.1.1. Synthesis of Sodium salt of Morpholinedithiocarbamic Acid 27
3.3.1.2. Synthesis of the RAFT Agent (PMD) 28
3.3.2. Preparation of ATRP ligand, Hexahexyl triethylenetetramine, H-TETA 28
3.3.3. Atom Transfer Radical Polymerization of Styrene 29
3.3.4. Transformation of Bromoalkyl End Group of ATRP Growth Poly(styrene) into Morpholinedithiocarbamate 29
3.3.5. Polymerization Kinetics of Styrene by using PMD as RAFT Agent 29
3.3.6. Polymerization of N-vinyl formamide by RAFT Method 30
3.3.7. Polymerization Kinetics of N-Vinylformamide by using PMD as RAFT Agent 30
3.3.8. Block Copolymerization 31
3.3.8.1. Block Copolymers Starting From Poly(N-vinylformamide) 31
3.3.8.2. Block Copolymers Starting From Poly(styrene) 31
3.3.9. Hydrolysis of Poly(N-vinylformamide) 32
3.3.10. Hydrolysis of N-vinylformamide Segments of the Block Copolymers 32

4. RESULTS and DISCUSSION 33
4.1. Synthesis of Homopolymers by RAFT Method 34
4.2. Preparation of Polystyrene by ATRP 38
4.3. Synthetic Strategy for the Block Copolymers 39
4.4. Properties of the Block Copolymers 39
4.5. Hydrolysis of PNVF and Block Copolymers 42

5. CONCLUSIONS 45

REFERENCES 46

AUTOBIOGRAPHY 56

LIST of ABBREVIATIONS

TPE	: Thermoplastic Elastomers
EO	: Ethylene oxide
PO	: Propylene oxide
PEO	: Poly(ethylene oxide)
PPO	: Poly(propylene oxide)
CMC	: Critical micelle concentration
CMT	: Critical micelle temperature
TEM	: Transmission electron microscopy
SANS	: Small angle neutron scattering
SAXS	: Small angle X-rey scattering
DLS	: Dynamic light scattering
SEC	: Size exclusion chromatography
NMR	: Nuclear magnetic resonance
ABC	: Amphiphilic block copolymer
PMAc	: Poly(methacrylic acid)
PS	: Polystyrene
THF	: Tetrahydrofuran
MPS	: Mononuclear phagocyte system
PBLA	: Poly(β-benzyl-L-aspartate)
PDLLA	: Poly(DL-lactic acid)
PCL	: Poly(ε-Caprolactone)
PMMA	: Poly(methyl methacrylate)
GTP	: Group transfer polymerization
ATRP	: Atom Transfer Radical Polymerization
ROMP	: Ring-opening Metathesis Polymerization
DT	: Degenerative transfer
RAFT	:Reversible Addition-Fragmentation Chain Transfer Polymerization
SFRP	: Stable free radical polymerization
MADIX	: Macromolecular design via interchange of xanthates
TEMPO	: 2,2,6,6-Tetramethyl-piperidinyloxy
LUMO	: Lowest unoccupied molecular orbital
MMA	: Methyl Methacrylate
PVAm	: Poly (vinyl amine)
PNVF	: Poly(N-vinylformamide)
NVF	: N-vinylformamide
NVA	: N-vinylacetamide
UV-Vis	: Ultraviolet – visible spectrophotometer
ESR	: Electron spin resonance
^{1}H-NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
FTIR	: Fourier Transformation Infrared Spectrophotometer
GPC	: Gel Permeation Chromatography
HPLC	: High Performance Liquid Chromatography

AIBN : 2,2'-Azoisobutyronitrile
MW : Molecular Weight
MWD : Molecular Weight Distribution
CRP : Controlled Radical Polymerization
PDI : Polydispersity Index
DMSO : Dimethyl sulfoxide
DMF : N,N-Dimethyl Formamide
NMP : 1-methyl-2-pyrrolidinone
PMD : Phenacyl morpholinedithiocarbamate
H-TETA : Hexahexyl triethylenetetramine
M : Monomer
St : Styrene
TETA : Triethylenetetramine

LIST of TABLES

		Page No
Table 2.1.	Experimental techniques for micelle characterization ….....	6
Table 4.1.	Viscosity records for PS and PS-*block*-PNVF ……	44

LIST of FIGURES

Page No

Figure 2.1 : Schematic representation of AB diblock copolymer micelles in a selective solvent of the A block 5
Figure 2.2 : Examples of nitroxides 18
Figure 2.3 : Representative examples of thiocarbonylthio RAFT agents … 19
Figure 2.4 : General structure of RAFT agents 21
Figure 4.1 : ^{1}H NMR of the RAFT agent (phenacyl morpholinedithiocarbamate) 35
Figure 4.2 : First order kinetics plot for RAFT polymerization of N-vinylformamide…… 36
Figure 4.3 : M_w – conversion plot of RAFT polymerization of N- vinylformamide …… 36
Figure 4.4 : First order kinetics plot for RAFT polymerization of styrene .. 37
Figure 4.5 : M_n — M_w/M_n vs. conversion plot for the poly(styrene) …… 37
Figure 4.6 : GPC chromatogram of poly(styrene) prepared by ATRP method …… 38
Figure 4.7 : ^{1}H NMR spectrum of block copolymer, which is started by PS and chain extended by NVF, in DMSO-d_6/DMF-d_7 ……... 40
Figure 4.8 : ^{1}H NMR spectrum of block copolymer, which is started by PS and chain extended by NVF, in trichloro acetic acid …….. 41
Figure 4.9 : FTIR spectra of homopolymers PNVF, PS and block copolymer PS-*block*-PNVF …… 42
Figure 4.10 : ^{1}H NMR spectra of PNVF and its hydrolysis product in D_2O .. 42
Figure 4.11 : ^{1}H NMR spectrum of hydrolysis product of block copolymer, which is started by PS and chain extended by NVF, in DMSO-d_6/DMF-d_7 ……. 43

LIST of SYMBOLS

$\mathbf{R}^{\cdot}$	**:** Radical
I	**:** Initiator
M	**:** Monomer
M_n	**:** Number average molecular weight
M_w	**:** Weight average molecular weight
M_w/M_n	**:** Molecular weight distribution
P_n^*	**:** Propagating species
M_t^n	**:** Transition metal
X	**:** Halide group
k_{act}	**:** Rate constant of activation
k_{deact}	**:** Rate constant of deactivation
k_{exch}	: Rate constant of exchange process
k_p	**:** Rate constant of propagation
C_{tr}	**:** Chain transfer constant
K_{eq}	**:** Equilibrium constant
k_t	**:** Rate constant of termination
M^m	: Molecular weight of micelle
M^u	: Molecular weight of unimer
Z'	: Aggregation number of the micelle
R_g	: Radius of gyration of the micelle
R_h	: Hydrodynamic radius of the micelle
R_c	: Micellar core radius
L	: Thickness of the shell of the micelle
Z	: Activating group in the structure of RAFT agent
R	**:** Homolytically leaving group in the structure of RAFT agent
$P_n^{\cdot}$, $P_m^{\cdot}$	**:** Active propagating species

CONTROLLED SYNTHESIS OF VINYL AMINE POLYMERS BY RAFT TECHNIQUE

SUMMARY

Vinyl amine polymers are key materials for functional polymers. Having easy transformation of the amino group these polymers are of great interest both in academia and industry. Since, vinylamine monomer does not exist these polymers are obtained by modification of suitable precurser polymers such as poly(N-vinylphtalimide) and poly(N-vinylacetamide) etc. Recently commercialized N-vinylformamide is the most important precursor for poly(vinylamine) at this time. This is the monomer radically polymerizable.

Block copolymer of poly(vinylamine) would be very useful to obtain copolymers having functional blocks. Such structures can be designed by controlled radical polymerization techniques. Among those ATRP is not suitable for controlled polymerization of N-vinylformamide. Another controlled radical polymerization technique RAFT seems to be applicable for polymerization of this monomer. To our best, there appear only few papers dealing with polymerization of the monomer by RAFT process. However, the high polydispersity (1,7 – 2,3) reported implies that the control of the chain growth has not been carried out successfully.

Since structure of the transfer agent is crucial for the chain growth control in RAFT process, in this study we have targeted to employ a new chain transfer agent, phenacyl morpholinedithiocarbamate, which was first introduced by our group for controlled polymerization of N-vinylformamide. The study is aimed at preparing block copolymers of poly(vinyl amine) with poly(styrene). This was performed by hydrolysis of poly(N-vinylformamide)-*block*-poly(styrene). In order to investigate controlled polymerization of N-vinylformamide and styrene monomers with this new RAFT agent, phenacyl morpholinedithiocarbamate, polymerization kinetics of each monomer was studied. In this study two methods were followed for preparation of N-vinylformamide – styrene block copolymers. In the first method, poly(N-vinylformamide was synthesized by RAFT method by using phenacyl morpholinedithiocarbamate RAFT agent. The resulting polymer was employed as macro transfer agent in the presence of AIBN for chain extension with styrene.

In the second route, poly(styrene) was prepared by ATRP method and the bromoalkyl end group of the polymer was transformed into morpholinedithiocarbamate function by action with sodium morpholinedithiocarbamate. By using this polymer as macro transfer agent N-vinylformamide was polymerized in the presence of AIBN to obtain poly(styrene)-*block*-N-vinylformamide.

The resulting polymers and block copolymers were characterized by ^{1}H NMR, GPC, FTIR and viscosimetry techniques.

VİNİL AMİN POLİMERLERİNİN RAFT YÖNTEMİ İLE KONTROLLÜ SENTEZİ

ÖZET

Vinil amin polimerleri, fonksiyonel polimerler için anahtar malzemelerdir. Vinil amin polimerleri, amino gruplarının kolayca reaksiyona uğratılabilmesi sebebiyle hem endüstriyel hem de akademik olarak büyük öneme sahiptir. Vinil amin monomeri mevcut olmadığından bunun polimerleri poli(N-vinilftalimid) veya poly(N-vinilasetamid) gibi uygun başlangıç polimerlerinin modifiye edilmesiyle elde edilebilmektedir. Yakın zamanda piyasaya sürülmüş olan N-vinilformamid monomeri vinil amin polimerlerinin en önemli başlangıç maddesidir. N-vinilformamid radikal yolla polimerleşebilen bir monomerdir.

Poly(vinilamin)in blok kopolimerleri fonksiyonel blok kopolimerin hazırlanması için çok önemlidir. Bu tür yapılar kontrollü radikal polimerizasyon yöntemleri ile sentezlenebilirler. Kontrollü radikal polimerizasyon yöntemleri içinde "atom transfer radikal polimerizasyonu" (ATRP), N-vinilformamidin polimerleştirilmesi için uygun değildir. Bir diğer kontrollü radikal polimerizasyon yöntemi olan "tersinir katılma-ayrılma zincir transfer polimerizasyonu" (RAFT) bu monomerin polimerleştirilmesi için uygun görünmektedir. Bilindiği kadarıyla, N-vinilformamidin RAFT metodu ile polimerleştirilmesine ilişkin az sayıda yayın yapılmıştır. Bu çalışmalarda molekül ağırlığı dağılımının oldukça yüksek olduğu (1,7 – 2,3) ve zincir büyümesinin kontrollü olmadığı görülmüştür.

RAFT metodunda, zincir transfer ajanının yapısı büyük önem taşıdığından, biz bu çalışmada, N-vinilformamidi RAFT metodu ile polimerleştirmede önce grubumuzca sentezlenmiş yeni bir transfer ajanı olan fenasil morfolinditiokarbamatı, kullanmayı hedefledik. Bu çalışmanın temel amacı poli(vinilamin) ve poli(stiren) blok kopolimerleri sentezlemektir. Bu blok kopolimerler poli(N-vinilformamid)-*blok*-poli(stiren) polimerlerinin hidrolizi yoluyla elde edilmiştir. N-vinilformamid ve stirenin bu yeni RAFT ajanı ile kontrollü polimerizasyonunu incelemek için bu monomerlerin polimerleşme kinetiği çalışmaları yapılmıştır. Burada poli(N-vinilformamid)-*blok*-poli(stiren) polimerlerini elde etmek için iki yol izlenmiştir. Birincisinde; fenasil morfolinditiokarbamat zincir transfer ajanı kullanılarak poli(N-vinilformamid) RAFT tekniği ile sentezlenmiştir. Elde edilen bu polimer makro transfer ajanı olarak kullanılarak stiren ile zincir uzatılarak blok kopolimer elde edilmiştir.

İkinci yolda ise; önce ATRP yöntemi ile poli(stiren) elde edilmiş, polimer ucundaki bromoalkil grupları morfolinditiokarbamik asidin sodyum tuzu ile reaksiyona uğratılarak morfolinditiokarbamat fonksiyonuna dönüştürülmüştür. Bu polimerin makro transfer ajanı olarak kullanılması ile AIBN varlığında N-vinilformamid ile zincir uzatma yapılmıştır.

Elde edilen polimer ve blok kopolimerler ^{1}H NMR, GPC, FTIR ve viskozimetre teknikleri ile karakterize edilmiştir.

1. INTRODUCTION

Amphiphilic block copolymers are important class of macromolecular architectures. Having both hydrophilic and hydrophobic groups, these macromolecules show interesting physicochemical behaviors in solutions. Self-organizing ability of amphiphilic block colpolymers makes them very useful for application in various fields such as controlled drug delivery [1], pharmaceutical formulations [2], solubilization of various inorganic or organic chemicals [3], etc.

Perhaps most important application of these materials is stabilization of nanoparticles and nanostructures. It has been realized that adsorption of one block selectively on insoluble particle surface is essential to prevent growth of the particles by coalescence. This effect is crucial for stabilization of the particles in nanometer sizes.

Moreover generation of nanoparticles in the presence of amphiphilic block copolymers results in monodispers particles with good stabilities. In recent years many research articles and reviews have been published on synthesis of various nanoparticles by using amphiphilic block copolymers [3,4].

Main difficulty in synthesis of nanoparticles is control of the particle size. When amphiphilic block copolymers are employed in stabilization of the nanoparticles it has been understood that the ratio and chain length of the blocks govern the particle sizes [5]. For this reason, preparation of well defined block copolymers is of particular interest for preparing of nanoparticles in controlled sizes.

However, adsorption of polymers on particle surfaces may not provide continuous stability in blending or in formulation of composite materials. Any external stimuli such as heat, electrical field or addition of a third component may induce destabilization of the particles and coalescence takes place inevitably. In order to provide permanent stabilities the block adsorbed on the surface need post crosslinking. These nanoparticles with permanent stability are so called “core-shell” nanoparticles [6]. The non-adsorbed blocks remaining at the outer surface allow compatibility of these materials with adequate base matrix.

It was considered that diblock copolymers constituting with reactive block such as poly(vinyl amine) would be very useful especially in preparation of inorganic hybrid nanoparticles. Since the amino group in the polymer is capable of coordination with many transition metal ions, these copolymers will be employed in preparation of core-shell nanoparticles in more direct way. Considering with those peculiarities of poly(vinyl amine), in this study, we have targeted to prepare poly(vinyl amine)-*block*-poly(styrene) by using N-vinylformamide monomer as source of poly(vinyl amine).

However, synthesis of amphiphilic block copolymers is very difficult task, in general, due to difficulty in finding suitable solvent capable of dissolving both of the blocks. Moreover, purification of the block copolymer needs tedious work up to obtain pure product free of homopolymers. These block copolymers can be prepared by living polymerization techniques. In order to obtain any desired block copolymer both of the monomers involved should be polymerizable by the same mechanism. This makes an important limitation for preparing block copolymers constituting with desired monomers. For instance, newly commercialized monomer, N-vinylformamide, is not polymerizable by ATRP technique. Although polymerization of this monomer by RAFT method has been reported, the molecular weight distributions attained were highly broad [7].

In this work, we have studied first polymerizabilities of N-vinylformamide and styrene by using phenacyl morpholinedithiocarbamate as chain transfer agent which was prepared in our laboratory. Thereafter, poly(N-vinylformamide) obtained was utilized as macro RAFT agent in polymerization of styrene monomer. Then poly(N-vinylformamide) block of the resulting polymer was hydrolyzed to give poly(vinyl amine)-*block*-poly(styrene). The polymers obtained in each step were characterized by conventional spectroscopic and chromatographic techniques.

In the second part of the study, poly(styrene) was prepared by ATRP and the bromoalkyl end group of the polymer was transformed into morpholinedithiocarbamate in order to chain extension with N-vinylformamide.

The results showed that both methods give expected block copolymers.

2. THEORETICAL PART

2.1. Block Copolymers

Block copolymers are composed of two or more covalently connected linear polymer segments with different composition. These may constitute with two or more segments and named diblock, triblock or multiblock copolymers accordingly. Various block copolymer architectures are possible including star-blocks and graft copolymers with two or more block arms [8].

2.1.1. Applications of Block Copolymers

The most important and popular application of block copolymers is their use as thermoplastic elastomers (TPEs). These materials are used for wine bottle stoppers, jelly candles, outer coverings for optical fiber cables, adhesives, bitumen modifiers, or in artificial organ technology.

The first commercial thermoplastic elastomers were produced by B. F. Goodrich Co. in the late fifties and were based on polyurethanes. The thermoplastic polyurethanes are linear multiblock copolymers (segmented block copolymers) forming hydrogen bonding between the urethane groups have excellent oil resistance and wear strength. These have found extensive use in manufacturing of automotive bumpers, snowmobile treads, etc.

In 1965 Shell introduced the styrenic thermoplastic elastomers under the trade name Kraton, which are polystyrene-b-polyisoprene(or polybutadiene)-b-polystyrene linear triblock co-polymers, made by anionic polymerization. In contrast to the polyurethane multi-block copolymers, the styrenic thermoplastic elastomers are well-defined materials with low molecular weights.

They are used in manufactoring of footwear, bitumen modification, thermoplastic blending, adhesives, and cable insulation and gaskets.

Block copolymers have found commercial applications as adhesives (both hot-melt and solution) and sealants, as blending agents for use with different homopolymers

for producing materials with desired characteristics, as surface modifiers of fillers and fibers in order to improve dispensability in the matrix, as surfactants for phase stabilization, as viscosity improvers of lubricating oils, as membranes for desalination, in biomedical applications, etc.

Block copolymers of ethylene oxide (EO) and propylene oxide (PO) have been commercialized by BASF.The linear PEO-b-PPO-b-PEO (Pluronic) or star structure $(PEO\text{-}b\text{-}PPO)_4$ (Tetronic) have found uses widely in the paper industry in cosmetics formulations etc. Due to the biocompatibility of polyethyleneoxide block, these materials are also of great interest in biomedical applications [9].

2.1.2. Amphiphilic Block Copolymers

There has been growing interest in the synthesis and characterization of amphiphilic block copolymers in recent years. Having both hydrophilic and hydrophobic blocks amphiphilic block are reminiscent of low molecular weight surfactants. Such amphiphilic copolymers find numerous applications as emulsifiers, dispersants, foamers, thickeners, and compatibilizers [3].

Perhaps most important aspect of amphiphilic block copolymers is their selforganizing ability via micellization. They form micelles above a concentration known as the critical micelle concentration (CMC).

However, it is known that block copolymers in selective solvents form spherical aggregates, with compact cores by insoluble blocks surrounded by soluble blocks. The micelles of block copolymers show an extremely narrow size distribution.

These micelles are generally spherical but may change in shape and size distribution under certain conditions [10,11].

Schematic representation of A–B diblock copolymer in a selective solvent for the A block is given in Fig-2.1. Such a micellar system is characterized by:

• the equilibrium constant unimers ↔ micelles

• the CMC and CMT, respectively, the critical micelle concentration and the critical micelle temperature

• the morphology which in the simplest case can be considered as spherical

• M^m; the molecular weight of the micelle

• Z'; the aggregation or association number, e.g. the average number of polymer chains in a micelle, deduced from M^m and the molecular weight M^u of the unimer with $Z' = M^m/M^u$.

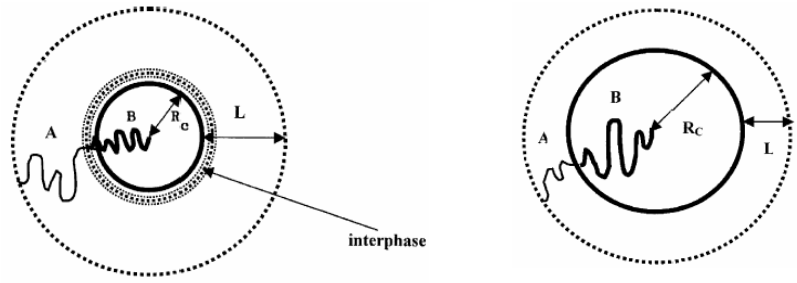
• R_g; the radius of gyration of the micelle

• R_h; the total hydrodynamic radius of the micelle

• the ratio R_g/R_h which is informative of the shape

• R_c; the micellar core radius

• L; the thickness of the shell (corona) formed by the soluble blocks. Micelles are given name as "hairy" micelle where $L » R_c$, and "crew-cut" micelle where $L < R_c$ (Fig-2.1.) [10].



"hairy" micelle $L » R_c$ "crew-cut" micelle $L < R_c$

Figure 2.1. Schematic representation of AB diblock copolymer micelles in a selective solvent of the A block. Rc : core radius; L : shell (corona) thickness [10].

There are various methods which can be classified in scattering, spectroscopic and in a wide range of other physical techniques for characterization of micelles. According to the listing provided by Chu and Zhou [12] the physical methods for the characterization of block copolymer micellar systems are summarized in Table 2.1.

Table 2.1. Experimental techniques for micelle characterization

Techniques	**Micelle characteristics**
TEM	Shape, size
SANS and SAXS	Molecular weight (weight-average), R_g; R_{core}; macrolattice structures
SLS	Molecular weight (weight-average), R_g
DLS	R_h
SEC	R_h; dynamics of micellar equilibrium
Ultracentrifugation	Micelle density, molecular weight (Z' average), micelle/unimer weight ratio
Fluorescence techniques	Chain dynamics, CMC, hybridization of micelles
NMR	Chain dynamics
Viscometry	R_h; intrinsic viscosity
Stop flow techniques	Kinetics of micelle formation and dissociation

Amphiphilic polymers have various applications some of which are summarized below.

2.1.2.1. Preperation of Nanoparticle Hybrids

Technologies have been developed that use components that are as small as possible, and size reduction of the constituent components plays an important role in the development of nanotechnologies. Characteristics of a material can strongly vary with the size and shape of the particles. Same material with same composition or molecular structure but different size can demonstrate different optical, magnetic, electric, adsorptive, catalytic, and other properties.

Amphiphilic block copolymers have an important role in the nanotechnological developments. For amphiphilic block copolymers, the notation "amphiphilicity" has a much broader meaning. ABC's not only stabilize oil/water interface, but stabilize any interface between different materials with different cohesion energies. As a consequence, these polymers can substitute low molecular weight surfactant molecules or extend surfactant applications such as stabilization of pigments. Owing

to capability of solubilizing or adhering to inorganic materials, amphiphilic block copolymers are of great importance for formation of nanoparticles. Förster et al. binded ZnO to PS-PMAc (poly (styrene)-poly(methacrylic acid)) block copolymers in THF, which is a common solvent for both PS and PMAc blocks [3].

2.1.2.2. Drug Delivery

Polymeric micelles are first proposed as drug carriers by Bader et al. [13] in 1984. Since they can solubilize poorly water soluble drugs in their inner core and they offer attractive characteristics such as a generally small size (< 100 nm) and a propensity to evade scavenging by the mononuclear phagocyte system (MPS) they became potential carrier for poorly water soluble drugs [14]. Micelles are often compared to natural occurring carriers such as viruses or lipoproteins [15, 16]. All three carriers demonstrate a similar core-shell structure that allows for their content to be protected while it is transported to the target cell.

Multiblock copolymers such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) have been described as potential drug carriers [17] due to thier self organization in micelles [18, 19]. Polymeric micelles employed in drug delivery purposes are mostly have hydrophobic core which generally consists of a biodegradable polymer such as poly(β-benzyl-L-aspartate) (PBLA) [20], poly(DL-lactic acid) (PDLLA) [21] or poly(Є-caprolactone) (PCL) [22]. Hydrophobic core serves as a reservoir for an insoluble drug and protects it from the aqueous environment. The core may also be hydrophilic (e.g. poly(aspartic acid). The core might be turned to be hydrophobic by association with oppositely charged polyions [23-25] or by hydrophobic interaction with the drug itself [26-28]. In several studies non- biodegradable polymers such as polystyrene (PS) [29, 30] or poly(methyl methacrylate) (PMMA) [31] have been also used as the inner core. These polymers impart interesting properties so that the micelle core becomes exceptionally stable due to glassy state of the core material. In order to be considered as drug carriers, nonbiodegradable polymers must be non-toxic or in low molecular weight to be excreted via the renal route [32].

2.1.2.3. Surfactant-based Applications

In many industrial and pharmaceutical preparations block copolymers are used as dispersants, emulsifiers, wetting agents, foam stabilizers, solubilizers, flocculants,

demulsifiers, etc, due to thier surface characteristics. Surfactants which are composed of ethylene oxide and propylene oxide blocks are the most widely used types of block copolymeric surfactants. Such block copolymers behave like typical hydrophobic-hydrophilic agents where the surface activity may be tailored just by adjusting the molecular characteristics. Because of their nontoxicity, ethylene oxide-propylene oxide block copolymers are used widely in cosmetics as dentifrices, mouthwashes, aerosol antiperspirant preparations, in the paper industry as transfer coatings, in the textile industry as antistatic agents, in agricultural formulations as dispersant for pesticides and as detergents, in the petroleum industry, and in water treatment [33].

Amphiphilic block copolymers are also used as stabilizers in the preparation of lattices. They are successfully employed in dispersion polymerization in aqueous and nonaqueous media [34]. Block copolymer stabilizers have special advantages compared to conventional surfactants mainly in dispersions or dispersion polymerization of hydrophobic particles in nonaqueous media, where the latter fail to stabilize the system. Besides their unique properties, they are also useful in water. It has been reported that styrene-ethylene oxide block copolymers [35] form stable polystyrene latex in water. Similarly styrene-isoprene block copolymers [36] form latex in dimethyl formamide.

2.1.3. Synthesis of Linear AB Diblock Copolymers

A variety of methods are applicable for synthesis of block copolymers. These will be described in detail in the following parts.

2.1.3.1. Block Copolymers by Anionic Polymerization

Living anionic polymerization is particularly suitable for the synthesis of block copolymers with well-defined structures. The absence of termination and chain transfer allows the preparation of chain segments and polymers with predictable molecular weights and narrow molecular weight distributions [37-39]. The living nature of these polymerizations means that block segments of known molecular weight can be prepared by sequential addition of monomers. The fact that the resulting block copolymers maintain their active anionic chain ends permits both postpolymerization chain end functionalization reactions and linking reactions to form linear and star-branched block copolymers [40]. Within the scope of monomers

which can be polymerized anionically without termination and chain transfer, anionic polymerization provides the most versatile and elegant methodology for the synthesis of block copolymers with controlled molecular weights, molecular weight distributions, composition and molecular architecture.

Some of the limitations of this method are that rigorous purification of monomers and solvents are usually required, and either high vacuum or inert-gas atmospheres are usually needed to exclude moisture and atmospheric contamination. The range of monomers which can be polymerized anionically without termination and transfer reactions includes styrenes, dienes, methacrylates, oxiranes (epoxides), thiiranes (episulfides) and cyclic siloxanes [41]. With certain monomers, especially those with polar functionalities some termination reactions may occur, however, this is not a drawback for them to be used to prepare the last-formed block in a sequence. In such cases control of molecular weight is not good. Monomers which have been polymerized anionically, but which do not necessarily produce living stable carbanionic chain-ends [41] include acrylonitriles [42,43], cyanoacrylates [44,45], 2-methyloxirane (propylene oxide) [46], vinyl ketones [47], acrolein [48], sulfonated monomers [49], vinylsilanes [50], halogenated monomers [51], carbonates [52] and lactones [53].

2.1.3.2. Block Copolymers by Cationic Polymerization

Cationic polymerization methodology has become important synthetic pathway to obtain tailor-made macromolecules after discovery of true living cationic polymerization of vinyl ethers by Higashimura et al. [54]. In recent years many investigations have demonstrated that almost all classes of cationically polymerizable vinyl and alkene type monomers can be polymerized in a controllable way [55-57]. The formation of polymers having predictable molecular weight and narrow molecular weight distributions gives unambiguous experimental evidence for elimination or suppression of termination and chain transfer reactions in these systems. These studies opened the way for block copolymer synthesis using cationically polymerizable monomers such as isobutylene, vinyl ethers, styrene and its derivatives with electron donating groups, N-vinylcarbazole, furan, and some other heterocyclic monomers, extending the range of block copolymers available for basic research and for possible technological applications [9].

The synthesis of linear block copolymers containing two chemically different blocks by cationic polymerization can be accomplished by sequential monomer addition in a simple and convenient way. The successful synthesis of diblock copolymers is based on the appropriate selection of experimental polymerization conditions, like Lewis acid, additives, solvent, and temperature. The most important part of the synthetic design is the selection of the appropriate order of monomer addition. Efficient crossover reaction occurs when the two monomers have almost equal reactivities or when the more reactive monomer is polymerized first followed by the addition of the less reactive. Monomer reactivity can be estimated using the nucleophilicity parameter [9, 56].

2.1.3.3. Block Copolymers by Living Free Radical Polymerization

Free radical polymerization is the oldest mechanism for polymerization of vinyl monomers [58]. A large range of monomers can be polymerized and copolymerized by free radical polymerization, under less rigorous experimental conditions compared with ionic polymerizations. However, due to termination and chain transfer reactions, the free radical mechanism is not suitable for preparation of polymers with low polydispersities.

Recent advances in free radical polymerization have led to the development of synthetic methods for eliminating or suppressing the undesired termination and chain transfer reactions [59].

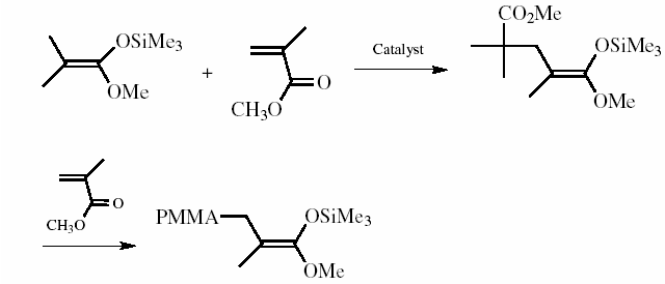
Diblock copolymers can be synthesized by living free radical polymerization with the technique of sequential monomer addition. The polymerization of the second monomer can be initiated by the macromolecular initiator already formed, in more or less the same way as it would be done in a normal homopolymerization [9].

Controlled/living radical polymerization techniques will be mentioned in detail in the following parts.

2.1.3.4. Block Copolymers by Group Transfer Polymerization

Group transfer polymerization (GTP) is a Michael-type catalyzed addition reaction [60-61]. A silyl ketene acetal is usually used as the initiator. As depicted in Scheme 2.1, the silane group is transferred to the growing chain end after the addition of each monomer unit which provides active chain ends until complete consumption of the

monomer. The molecular weight of the polymer prepared can be adjusted by the amount of the initiator and the monomer used, since the polymerization is living. This type of polymerization reaction has been widely applied to the polymerization of (meth)acrylic monomers bearing side groups, which are sensitive to ionic or radical polymerization reactions [62]. Although GTP has the tolerance to certain functionalities such as tertiary amines, epoxides, styrenic, and allylic groups, this polymerization method is not suitable for monomers with functionalities like -OH and -COOH groups. The monomers in the latter class can be polymerized after protection with appropriate protective groups. Deprotection after polymerization gives access to hydrophilic polymers.



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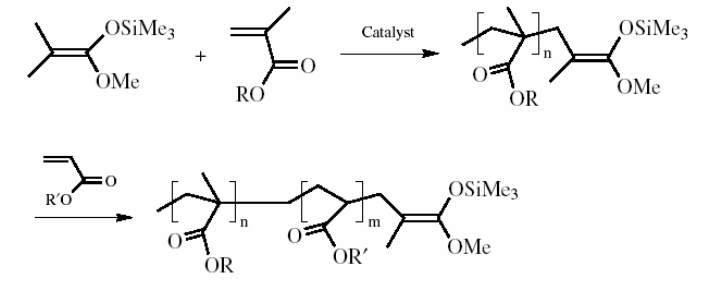


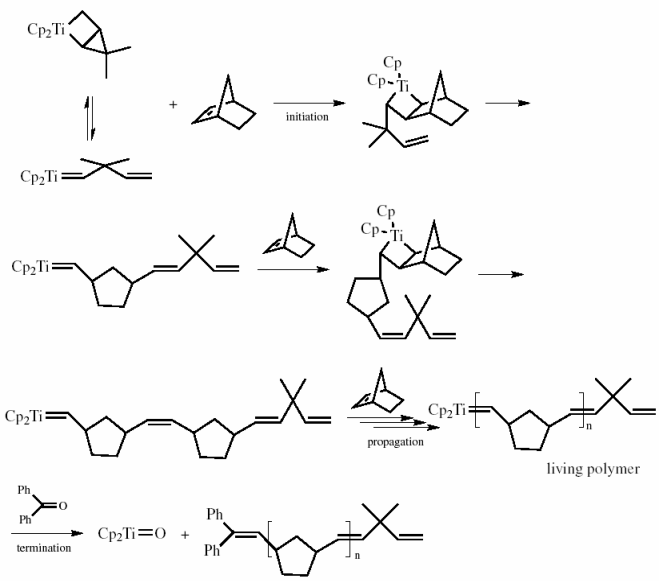
(2.2)

By group transfer polymerization a number of monomers can be polymerized. The main advantage of GTP is that, it has the ability to polymerize some monomers which can not be polymerized by any other method. This opens the way of preparation of new block copolymers. Another advantage of GTP is the relative ease in the polymerization of (meth)acrylate monomers when compared with anionic polymerization. GTP can be performed in room temperatures. Diblock copolymers can be synthesized by a two-step sequential monomer addition as depicted in Scheme 2.2. When a diblock copolymer consisting of one methacrylate block and one

acrylate block has to be synthesized, polymerization starts from the less reactive methacrylate monomer followed by the polymerization of the acrylate type monomer, since the dialkylsilane ketene acetal group that is formed at the end of the methacrylate block is more reactive compared with the monoalkyl silane ketene acetal groups present at the end of the acrylic block [60].

2.1.3.5. Block Copolymers by Ring Opening Methathesis Polymerization

Lately, ring opening metathesis polymerization (ROMP) becomes very useful method for the polymerization of a wide variety of strained cyclic alkene monomers [63]. ROMP is a transition-metal-mediated living polymerization technique. However, livingness is dependent on the proper choice of transition metal initiator, coinitiator, and other experimental conditions. The polymerization of norbornene with titanacyclobutane complexes is typical example for ROMP described in the literature [64, 65].



(2.3)

The metalcyclobutane is in equilibrium with its ring-opened carbene form as shown in Scheme 2.3. Polymerization goes through the ring opened structure. Propagation proceeds until the monomer is completely consumed, without any side reactions. By adding a ketone or an aldehyde deactivation of the metal site takes place and thus polymerization stops. Other types of initiators based on tungsten and molybdenum complexes have been reported [66, 67]. Ruthenium-based complexes have also been used as ROMP initiators [68, 69]. Some of these complexes require the presence of a

Lewis acid as a cocatalyst for increased activity (e.g., $W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2X_2$, where X = halide). Their reactivity can be controlled to a certain extent by the nature of the ligands [70].

Because a number of substituted and nonsubstituted strained cycloalkene monomers can be polymerized in a living manner by ROMP, the synthesis of a variety of block copolymers based on these monomers can be accomplished. Synthesis of diblock copolymers by ROMP is possible through two-step sequential addition of monomers. The course of the copolymerization reactions can be followed by ^{1}H-NMR in many systems [9].

2.1.3.6. Block Copolymers by Combination of Different Polymerization Methods

Since each polymerization method is not suitable for any kind of monomer, there are some limitations in preparing block copolymers if only one polymerization method is considered for the synthesis. However, transformation of polymerization mechanisms gives the opportunity to prepare block copolymers which are composed of monomers polymerizable with different methods.

Some of the transformation mechanisms can be accounted as anionic polymerization to cationic polymerization, Ziegler-Natta polymerization or radical polymerization; cationic polymerization to anionic polymerization or radical polymerization; radical polymerization to anionic polymerization or cationic polymerization; ring opening metathesis polymerization to radical polymerization or group transfer polymerization; Ziegler-Natta polymerization to radical polymerization or cationic polymerization [9, 71].

2.1.3.7. Block Copolymers by Chemical Modification

In order to synthesize block copolymers a wide variety of monomers can be polymerized by one polymerization method or a combination of different polymerization methods. However, synthesizing well-defined block copolymers require living polymerization processes which actually limits the range of monomers to be employed. This limitation arises especially when the monomers have functional groups. A possible way to overcome this problem is protecting the functional group with a proper protecting group with respect to functional group and polymerization mechanism.

Another way of solving the problem of synthesizing block copolymers, consisting of monomers that are difficult to polymerize by a living mechanism, is to employ polymer-analogous reactions. In this general methodology, a well-defined and suitably chosen precursor polymer is chemically transformed into another polymer by making use of well-known organic reactions. Because the chemical nature of the polymer will be altered, its properties will also differ from those of the precursor. When block copolymers are considered, chemical modification can be performed on one of the blocks selectively, using the appropriate chemical route, or on the whole copolymer. Sequential modification of each block is also possible if the order of chemical transformation of each block and the reaction conditions employed each time have been chosen judiciously.

This synthetic methodology should be performed under relatively mild, but effective, reaction conditions. During transformation of the precursor block to a new one, having the desired chemical nature and properties, there would not be any degradation, crosslinking, and, in general, any side reactions that can deteriorate the other molecular characteristics of the copolymer. When the precursor block copolymer has been chosen, the number of segments in the new copolymer and in each block is automatically chosen, as well as its molecular architecture. These molecular characteristics, together with the molecular weight distribution, should normally remain unaltered.

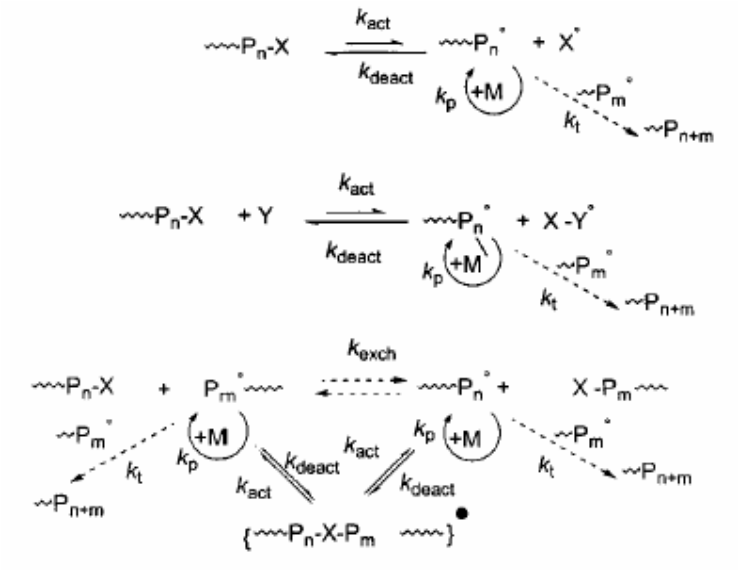
Some of the polymer-analogous reactions are hydrogenation, hydrolysis, quaternization, sulfonation, hydroboration/oxidation, epoxidation, chloro/bromoethylation and hydrosilylation [9].

2.2. Controlled/Living Radical Polymerization

The synthesis of polymers with well defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. For this purpose living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination [72-74]. Until the development of controlled/living radical polymerization methods living polymerizations were performed by anionic, cationic, coordination, and ring-opening polymerizations. Since controlled/living radical polymerization methods are more tolerant to functional groups and impurities, they find place in industry [75]. The

concept of living radical polymerization was originally introduced by Otsu in the early 1980s through his extensive investigation of iniferters [76, 77].

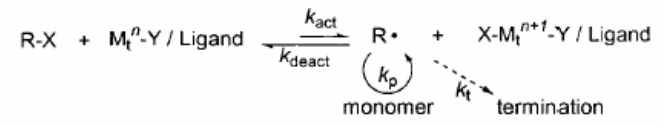
In the recent years, there was a great development in controlled/living polymerization methods. Controlled/living radical polymerization methods are based on establishing a rapid dynamic equilibration between a low amount of growing free radicals and a large majority of the dormant species. The dormant species are alkyl halides in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters in reversible addition fragmentation chain transfer processes (RAFT), alkoxyamines in nitroxide mediated polymerization or stable free radical polymerization (SFRP) [78, 79].



All of the CRP methods, shown in Scheme 2.4., include activation and deactivation steps (with rate constants k_{act} and k_{deact}), although in RAFT and DT the scheme may be formally simplified to just the exchange process with the apparent rate constant k_{exch}. Generated free radicals propagate and terminate (with rate constants k_p and k_t), as in a conventional free-radical polymerization. Thus, although termination occurs, under appropriate conditions its contribution will be small (less than a few percent of total number of chains) and these radical polymerizations behave as nearly living or controlled systems [80].

2.2.1. Atom Transfer Radical Polymerization (ATRP)

The first invention of atom transfer radical polymerization (ATRP) dates back to 1995. ATRP method was introduced by Sawamoto [81], Matyjaszewski [82] and Percec [83].



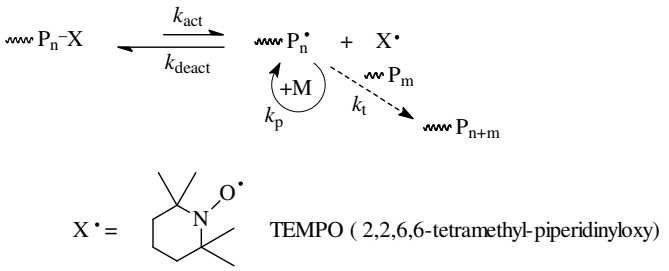
(2.5)

A general mechanism for ATRP shown in 2.5 corresponds to case b of Scheme 2.4. The radicals, or the active species, are generated through a reversible redox process catalyzed by a transition metal complex (M_t^n-Y/Ligand, where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, R-X. This process occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, $X\text{-}M_t^{n+1}$, as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination [84]. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [85, 86].

2.2.2. Nitroxide Mediated Polymerization

Nitroxide mediated polymerization dates back to late 1970s and early 1980s. It was first introduced by the radical trapping work of Rizzardo and Solomon [87-93]. Most of those works was about initator derived radicals. However, under the lights of those works, it has been realized that alkoxyamines have the potential to be utilized for polymer growth. Fundamental understanding of the activation-deactivation cycle in nitroxide mediated polymerization was understood in 1990 [94]. Controlled polymerization of styrene in the presence of benzoyl peroxide and the mediating stable free radical TEMPO (2, 2, 6, 6-tetramethyl-1-piperidynyl-N-oxy) was the mile-stone of today's controlled radical polymerization [95]. Polystyrene molecular weights evolved linearly with conversion and polydispersities were below 1.3 in this reaction, conducted at 120°C.



(2.6)

Control in nitroxide mediated polymerization is achieved with dynamic equilibration between dormant alkoxyamines and actively propagating radicals (Scheme 2.6). In order to effectively mediate polymerization, TEMPO (and other stable free radicals) should neither react with itself nor with monomer to initiate the growth of new chains, and it should not participate in side reactions such as the abstraction of β-H atoms. These persistent radicals should also be relatively stable, although their slow decomposition may in some cases help maintain appropriate polymerization rates [96].

Since TEMPO and its derivatives form a relatively strong covalent bond in alkoxyamines, the equilibrium constant (ratio of dissociation (k_{act}) to cross-coupling/association (k_{deact}) rate constant) is generally very small, i.e., $k_{act}/k_{deact} = K_{eq} \approx 1.5 \times 10^{-11}$M at 120°C for styrene [97]. The values of K_{eq} are often so low that in the presence of excess TEMPO, the equilibrium becomes very strongly shifted towards the dormant species and significantly reduces the polymerization rate. While

original TEMPO-based systems were successful at controlling the polymerization of styrene and some of its copolymers, they failed to mediate polymerization of acrylates and several other monomers for this reason.

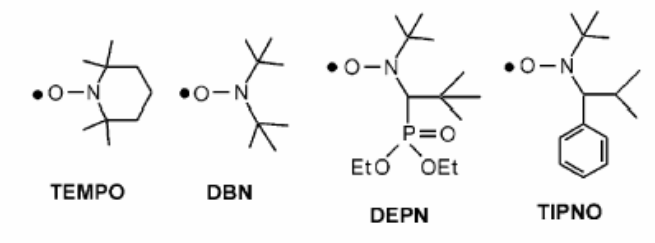


Figure 2.2. Examples of nitroxides

Polymerization could in principle be accelerated (i.e., the concentration of growing radicals could be increased) if the concentration of TEMPO were reduced. This might be accomplished by the slow self-destruction of nitroxide by a reaction with additives or initiating radicals [98-100]. This occurs spontaneously in the polymerization of styrene due to thermal self-initiation at elevated temperatures.

Some examples of nitroxides employed in nitroxide mediated polymerization are given in Fig-2.2.

2.2.3. Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT)

Reversible addition fragmentation chain transfer polymerization was discovered by the CSIRO (Commonwealth Scientific & Industrial Research Organization) team led by Ezio Rizzardo in 1998 [101]. Reversible addition–fragmentation chain transfer (RAFT), is the most successful among controlled radical polymerization methods due to its applicability to a wide range of monomers. Exchange reactions in this technique are also very fast, which lead to well controlled systems. RAFT polymerization uses thiocarbonylthio compounds, in order to mediate the polymerization via a reversible chain transfer process. Representative examples of thiocarbonylthio RAFT agents are shown in Fig-2.3. [102]

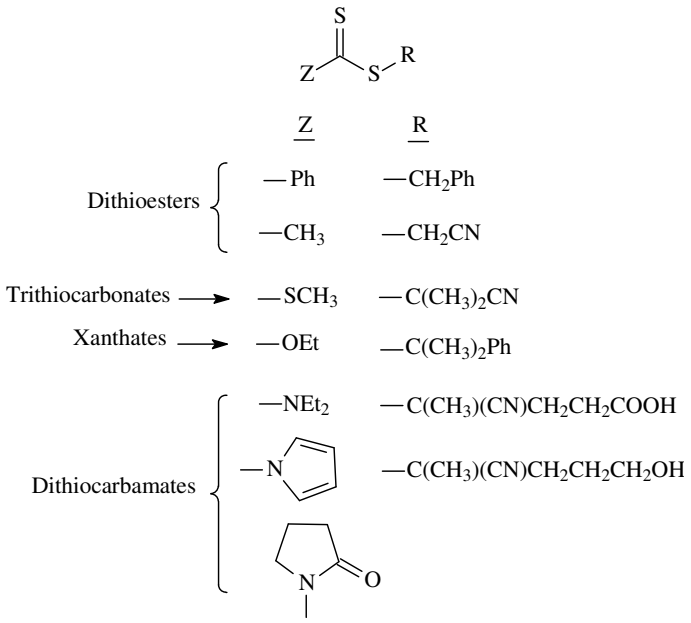


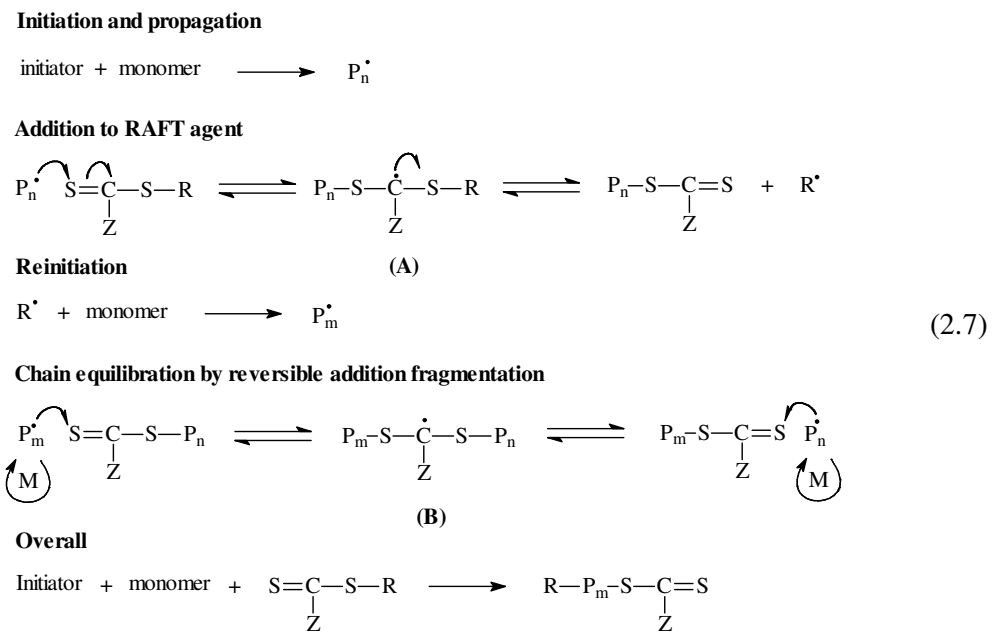
Figure 2.3. Representative examples of thiocarbonylthio RAFT agents. [102]

There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: (1) dithioesters (Z=aryl or alkyl), (2) trithiocarbonates (Z=substituted sulfur), (3) dithiocarbonates (xanthates) (Z=substituted oxygen), and (4) dithiocarbamates (Z=substituted nitrogen). A report of a controlled free radical polymerization technique involving xanthates, referred to as MADIX (***ma***cromolecular ***d***esign via ***i***nterchange of ***x***anthate), has been described [103].

RAFT polymerization is performed by adding a chosen quantity of an appropriate RAFT agent (Fig-2.3) to a conventional free radical polymerization mixture and yields polymers of predetermined chain length and narrow polydispersity. Polydispersity indices of less than 1.1 can be usually achieved under optimal conditions. The RAFT process offers the same versatility and convenience as convention free-radical polymerization being applicable to the same range of monomers (e.g., (meth)acrylates, styrenes, acrylamides, vinyls), solvents, functional groups (e.g. OH, CO_2H, NR_2, NCO) and reaction conditions (e.g., bulk, solution, suspension and emulsion). The RAFT process yields thiocarbonylthio-terminated polymers (or 1,1-disubstituted alkene-terminated oligomers if macromonomers are used as RAFT agents) that can be chain extended to yield a variety of copolymers (e.g., AB, ABA blocks, gradient, segmented) [102].

The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition-fragmentation steps as depicted in Scheme 2.7. As for conventional free-radical polymerization, initiation by decomposition of an initiator leads to formation of propagating chains. In the early stages, addition of a propagating radical (P_n•) to the RAFT agent [S=C(Z)SR] followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical (R•).

The radical R• reinitiates polymerization by reaction with monomer to form a new propagating radical (P_m•). In the presence of monomer, the equilibrium between the active propagating species (P_n• and P_m•) with the dormant polymeric RAFT compound provides an equal probability for all the chains to grow. This feature of the RAFT process leads to the production of narrow polydispersity polymers. When the polymerization is complete, the great majority of the chains contain the thiocarbonylthio moiety as the end group (Scheme 2.7) which has been identified by ^{1}H-NMR and UV-vis spectroscopy [101]. Additional evidence for the proposed mechanism was provided by the identification of the intermediate thioketal radical (A and/or B, Scheme 2.7) by ESR spectroscopy [104].



(2.7)

In order for the RAFT process to function effectively there are certain aspects of the polymerization conditions that require consideration. The most critical considerations are choice of the RAFT agent and an appropriate rate of initiation.

The RAFT agent must be chosen such that its chain transfer activity is appropriate to the monomers to be polymerized. The electronic properties of the Z group and the stereoelectronic properties of the R group determine the chain transfer activity of the RAFT agents (Fig-2.4). The Z group in the RAFT agent influences the reactivity of the double bond. As such, the Z group must be chosen so that it activates the double bond toward radical addition but at the same time not provide too great a stabilizing influence on the adduct radical (as this will contribute to slow fragmentation and hence retardation) Similarly, the R group must be chosen such that it is a good radical leaving group relative to the radical of the propagating species [101, 105]. The leaving group R• should also preferentially add to monomer.

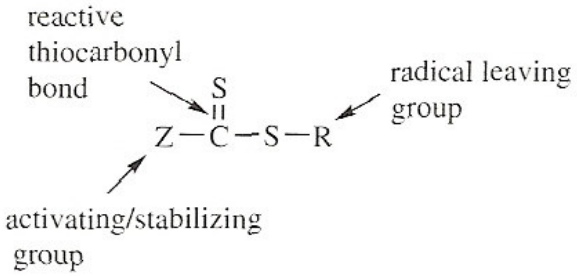


Figure 2.4. General Structure of RAFT Agents

The effect of various Z groups on the chain transfer activity of RAFT agents has been discussed in a published report [106]. By keeping the R group constant, a direct correlation between the chain transfer activity and the reactivity of the C=S bond was observed. The change in the reactivity of the C=S bond was related to the heats of reaction for C=S addition and the LUMO energies [106]. For the RAFT polymerization of styrene, the chain transfer constants were found to decrease in the series where Z is aryl (Ph) » alkyl (CH_3) ~ alkylthio (SCH_2Ph, SCH_3) ~ N-pyrrolo » N-lactam > aryloxy (OC_6H_5) > alkoxy » dialkylamino.

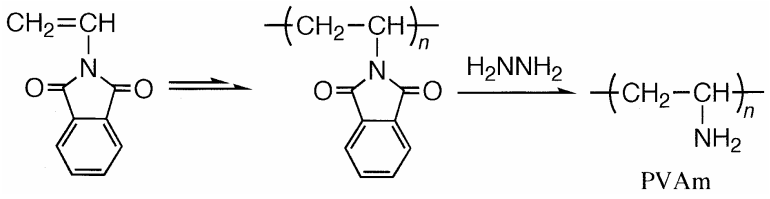
In a parallel study the Z group was kept constant and the effect of the R group on the chain transfer activity of RAFT agents was investigated [105]. It was reasoned that the C_{tr} should reflect the effect of the R group on the partitioning of the intermediate adduct radical between starting material and product (see Scheme 2.7). In the RAFT

polymerization of MMA with dithiobenzoates [S=C(Ph)SR], the effectiveness of the RAFT agent (i.e., the leaving group ability of R) decreases in the order: $C(alkyl)_2CN$ ~ $C(alkyl)_2Ph$ > $C(CH_3)_2C(=O)OEt$ > $C(CH_3)_2C(=O)$ NH(alkyl) > $C(CH_3)_2CH_2C(CH_3)_3$ ~ $CH(CH_3)Ph$ > $C(CH_3)_3$ ~ CH_2Ph. In reality, only the first two groups are effective in preparing poly(MMA) of narrow polydispersity (M_w/ M_n = 1.1) and predetermined molecular weight.

2.3. Poly(vinylamine)s

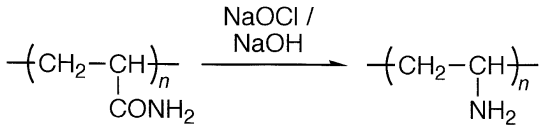
Polymers bearing primary amine functionalities are of great interest because of their high reactivity for various postderivatization reactions as well as their cationic nature in appropriate pH regimes [107]. There are numerous applications for cationic polymers, especially for poly(vinylamine) (PVAm) because of the high charge density and high reactivity of the primary amine-pendant groups. Papermaking [108], wastewater treatment [109], metal complexation [110], and petroleum production [111] are only a few industrially relevant processes involving PVAm. Also, the physiological compatibility of PVAm materials is important for their use in biological applications that is, as a support for enzymes or other active components. The cationic forms in particular show excellent adhesion to anionically charge biological surfaces, such as cellulose, skin, and hair [112, 113].

Monomeric vinylamine is unstable, and poly(vinylamine) (PVAm) cannot be synthesized in one step. However, various attempts to synthesize poly(vinylamine) by using different polymeric precursors have been made during the past 50 years [114]. The first synthesis of well-defined poly(vinylamine) was achieved by the polymerization of *N*-vinylphthalimide, followed by hydrolysis with hydrazine (Scheme 2.8) [115].



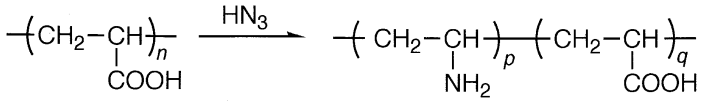
(2.8)

The conversion of poly(acrylamide) into poly(vinylamine) by the Hoffman reaction has been investigated extensively (Scheme 2.9) [116-120]. This method is very attractive because of the low cost of poly(acrylamide). In early reports, the conversion into amino groups was low and side reactions occurred [116]. Tanaka investigated the reaction condition in detail and found that the use of a large excess of sodium hydroxide and a low reaction temperature suppressed the undesirable side reaction to produce poly(vinylamine) with more than 90% purity [117, 118]. The detailed reinvestigation of the reaction conditions increased its purity to 95% [119].



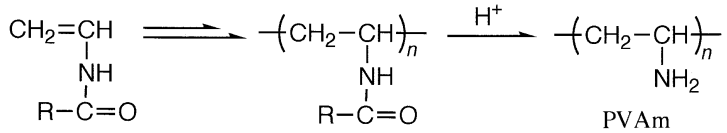
PVAm (2.9)

The synthesis of poly(vinylamine) from poly (acrylic acid) by the Schmidt reaction was also attempted (Scheme 2.10) [121]. The conversion reaction proceeded in only 50–60%, yielding a polyampholyte.



(2.10)

Recently, preparation of poly(vinylamine) on an industrial scale has been achieved successfully with the development of a precursor synthesis. N-vinylformamide (NVF) and N-vinylacetamide (NVA) were polymerized radically, followed by acid hydrolysis to produce poly(vinylamine) hydrochloride (Scheme 2.11) [122-123]. Poly(N-vinylformamide) was converted into poly(vinylamine) under milder conditions than was poly(N-vinylacetamide).



NVF (R=H)
NVA (R=CH_3)

PVAm (2.11)

Water-soluble poly(N-vinylformamide) (PNVF) has become more available in the past decade due to the development of improved processes for synthesis and purification of the N-vinylformamide (NVF) monomer as well as the growing uses

for PNVF and its derivatives in industrial applications [112]. The polymer has been proposed as a replacement for toxic acrylamide polymers [124] for industrial use.

3. EXPERIMENTAL WORK

3.1. Materials and Chemicals

Monomers and some of the solvents are purified prior to use. Unless otherwise stated, chemicals are used as they are purchased.

3.1.1. Monomers

N-vinylformamide (Aldrich): Vacuum distilled prior to use.

Styrene (Aldrich): Washed with 10% NaOH solution and rinsed with distilled water. Dried with Na_2SO_4.

3.1.2. Solvents

Monoethylene glycol (technical grade) was distilled under vacuum before use. It was used as solvent in preparation of PNVF.

Ethylene glycol monomethyl ether (E. Merck): Vacuum distilled prior to use. It was used as solvent in preparation of PNVF.

1-methyl-2-pyrrolidinone (NMP) (Aldrich): It was used as solvent in preparation of PNVF-*block*-PS.

1,4-Dioxane (Labscan): It was used as solvent in preparation of PS by RAFT method.

Acetone (E. Merck): It was used for precipitation of N-vinylformamide homopolymer and block copolymers of N-vinylformamide and styrene, which were based on N-vinylformamide homopolymers.

Methanol (Labscan): It was used for the precipitation of styrene homopolymer and block copolymers of styrene and N-vinylformamide, which were based on styrene homopolymers.

Diethyl ether (E. Merck): It was used for precipitation of morpholinedithiocarbamic acid sodium salt.

Ethanol (E. Meck): It was used for preparation of ATRP ligand.

Tetrahydrofuran (E. Merck): It was used for preparation of ATRP ligand.

Ethyl acetate (Labscan): It was used for preparation of ATRP ligand.

N,N-dimethylformamide (DMF) (E. Merck): It was used for preparation of block copolymer solutions.

Dimethylsulfoxide (DMSO) (E. Merck): It was used for preparation of block copolymer solutions.

DMF-d_7 (E. Merck): It was used as solvent for ^{1}H-NMR measurements.

DMSO-d_6 (E. Merck): It was used as solvent for ^{1}H-NMR measurements.

3.1.3. Other Chemicals

AIBN 2, 2'-Azobisisobutyronitrile (Fluka): It was used as initiator in RAFT polymerizations.

LiCl (E. Merck): Used for preparing magic solvent together with NMP.

Morpholine (Aldrich): Used for preparation of sodium salt of morpholinedithiocarbamic acid.

Carbondisulfide (E. Merck): Used for preparation of sodium salt of morpholinedithiocarbamic acid.

Sodium hydroxide (NaOH) (E. Merck): Used for preparation of sodium salt of morpholinedithiocarbamic acid and for hydrolysis.

Phenacyl bromide (Aldrich): It was used for synthesis of phenacyl morpholinedithiocarbamate.

Triethylenetetramine (TETA) (Fluka): This was used in preparation of ATRP ligand.

1-Bromohexane (Aldrich): Used during preparation of ATRP ligand.

Benzyl bromide (E. Merck): It was used as ATRP initiator.

Copper (I) bromide (CuBr): This was freshly prepared according to the procedure described in the literature [125] and used as ATRP catalyst.

3.2. Equipments

3.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analysis was recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed with a set up consisting of an Agilent 1100 RI apparatus equipped with three Waters ultrastyragel columns (HR 5E series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 ml/min and a refractive index detector. Molecular weights were calculated by using monodisperse polystyrene standards.

3.2.3 High Performance Liquid Chromatography (HPLC)

For determination of molecular weight of water soluble polymers HPLC Shimadzu LC-10AD with 300*7.8mm Gdgda-gdma columns was used. Eluent was water. The detector was refractive index detector (RID). Fructose standards were used for calibration.

3.2.4. Fourier Transformation Infrared Spectrophotometer (FTIR)

IR spectra were recorded on a Perkin Elmer Spectrum One B FT-IR spectrophotometer.

3.2.5. Ubbelohde Viscometer

Viscosity measurements of polymers and block copolymers were performed in 1:1 DMF: DMSO mixture by capillary viscosimetry technique using Ubbelohde viscometer at 25°C.

3.3. Synthetic Procedures

3.3.1. Praparation of RAFT Agent, Phenacyl Morpholinedithiocarbamate (PMD)

3.3.1.1. Synthesis of Sodium Salt of Morpholinedithiocarbamic Acid

To a 100 ml volume of Erlenmayer flask equipped with a dropping funnel, there were added 17.4 g (0.2 mol) morpholine and 20 ml methanol. The solution was cooled in

an ice bath and 7.6 g (0.1 mol) carbon disulfide was then added drop wise via the dropping funnel over a period of 1 h, while stirring. The stirring was continued for additional 1 h and the solution of 4 g (0.1 mol) NaOH in 20 ml methanol was added to the mixture. The reaction content was heated at 60 °C for 1 h and about 3 /4 of methanol was removed by rotavapor. After cooling, 40 ml of diethyl ether was added to the flask for precipitation of sodium salt of morpholinedithiocarbamic acid. White precipitate was collected by filtration and dried under vacuum at 40°C overnight. The yield was 15.7 g (84.9 %).

3.3.1.2. Synthesis of the RAFT Agent (PMD)

Sodium salt of morpholinedithiocarbamic acid (11.1 g, 0.06 mol) was dissolved in 35 ml methanol. Then methanol solution (20 ml) of phenacyl bromide (11.9 g, 0.06 mol) was added to this solution and the mixture was stirred with a magnetic stirring bar for 24 h at room temperature. The stirring was continued at 60°C for 1 h. The turbid solution was poured into 200 ml of distilled water. The white crystalline mass was filtered and dried under vacuum for 16 h. Yield 11.6 g (68.8 %), mp: 129.5°C.

3.3.2. Preparation of ATRP Ligand, Hexahexyl triethylenetetramine (H-TETA)

Preparation of the ATRP ligand, H-TETA was performed according to literature [126] as follows:

Triethylenetetramine (TETA) was alkylated with 1-bromohexane (3.2) as follows. TETA was distilled (167–171°C/1 Torr) before use. 1-Bromohexane (43 ml, 0.305 mol) was added to a solution of 7.3 ml (0.05 mol) of TETA in 50 ml of ethanol and stirred for 1 h at room temperature. Potassium carbonate powder (K_2CO_3, 55 g, 0.4 mol) was added to the mixture and refluxed for 72 h under continuous stirring. While hot, the mixture was filtered and washed with 40 ml of ethanol. The filtrate was transferred into the reaction flask, and another 55 g of K_2CO_3 were added to the mixture. The mixture was refluxed for another 72 h. After cooling, the reaction content was poured into 300 ml of water in a separatory funnel. The organic layer was separated with 70 ml of ethyl acetate. The organic phase was dried with 25 g of anhydrous Na_2SO_4 and filtered. The ethyl acetate in the filtrate was removed on a rotavapor. The product was further purified by column chromatography (with basic aluminum oxide, activated, Aldrich, Brockmann I, standard grade, 150 mesh) with 80

ml of dry tetrahydrofuran (THF). Removal of the THF on a rotavapor gave a light yellow oil. The viscous oily product weighed 21.8 g (86.0%).

3.3.3. Atom Transfer Radical Polymerization of Styrene

A 100 ml of three-necked flask was mounted on thermostated oil bath. The flask was equipped with a reflux condenser and a nitrogen inlet. Then 1.95 g ($3x10^{-3}$ mol) of H-TETA ligand, 0,43 g ($3x10^{-3}$ mol) CuBr and 34.5 ml (0.3 mol) styrene were charged to the flask under nitrogen stream. The nitrogen flow was continued for 15 min. The oil bath was preheated to 90°C. 0.36 ml ($3x10^{-3}$ mol) of benzyl bromide was added to this mixture, nitrogen flow was continued for additional 5 min and flask was placed in oil bath. The mixture was stirred continuously with a magnetic bar. After 15 h reaction time, the polymer was precipitated in 250 ml water. Precipitated polymer is dissolved in THF and dried with Na_2SO_4. Polymer solution was filtered and 2 ml of HNO_3 was added to the solution. Polymer was precipitated into 500 ml 3% acetic acid solution. Precipitated polymer was dissolved and precipitated again in the same way. Obtained polymer was filtered and dried at 60°C under vacuum overnight. Yield was 60 %.

3.3.4. Transformation of Bromoalkyl End Group of ATRP Growth Polystyrene into Morpholine Dithiocarbamate

Polystyrene (2 g) prepared by ATRP method (M_n : 8000, PDI: 1.14) was dissolved in 10 ml of NMP. Then the solution of 3 g morpholinedithiocarbamic acid sodium salt in 10 ml NMP was added to the above solution and the mixture was heated at 85°C for 15 hours under reflux condenser. The polymer was precipitated in 50 ml of NaCl solution (5%) and filtered. The product was dried under vacuum at 60°C for overnight. 1.8 g product was obtained.

3.3.5. Polymerization Kinetics of Styrene by using PMD as RAFT Agent

A 100 ml of three-necked flask was mounted on thermostated oil bath. The flask was equipped with a reflux condenser and a nitrogen inlet. Then 28 g of 1, 4-dioxane, 12 g (0.1154 mol) of styrene and 0.324 g ($1.15x10^{-3}$ mol) of phenacyl morpholinedithiocarbamate were charged to the flask under nitrogen stream. The nitrogen flow was continued for 15 min. The oil bath was preheated to 60°C. 0.076 g ($0.46x10^{-3}$ mol) of AIBN was added to this mixture, nitrogen flow was continued for

additional 5 min. and flask was placed in oil bath. The mixture was stirred continuously with a magnetic bar. To follow kinetics of the polymerization, samples (approx. 2 ml) were withdrawn via pipette at appropriate time intervals, to inspect the polymerization yields. The polymer samples were isolated by precipitation in 17 - 18 ml methanol. The samples were centrifuged and solvent was decanted. Vacuum-dried samples were weighed and percentage polymer contents of the samples were used to build up of conversion-time plot (Fig-4.4).

3.3.6. Polymerization of N-vinylformamide by RAFT Method

A 250 ml of three-necked flask was mounted on thermostated oil bath. The flask was equipped with a reflux condenser and a nitrogen inlet. Then 42.6 g of monoethylene glycol, 42.6 g of ethylene glycol monomethyl ether, 42.6 g (0.6 mol) of N-vinylformamide and 1.686 g ($6x10^{-3}$ mol) of phenacyl morpholinedithiocarbamate were charged to the flask under nitrogen stream. The nitrogen flow was continued for 15 min. The oil bath was preheated to 60°C. 0.394 g ($2.4x10^{-3}$ mol) of AIBN was added to this mixture, nitrogen flow was continued for additional 5 min. and flask was placed in oil bath. The mixture was stirred continuously with a magnetic bar. After approximately 40 hour reaction time the polymer was precipitated in 500 ml acetone, filtered and dired overnight at 50°C under vacuum. Yield was 47 %

3.3.7. Polymerization Kinetics of N-vinylformamide by using PMD as RAFT Agent

The polymerization kinetics were carried out in ethylene glycol monomethyl ether and ethylene glycol mixture with 37.5 % total monomer concentration. A typical procedure is as follows:

A 100 ml of three-necked flask was mounted on thermostated oil bath. The flask was equipped with a reflux condenser and a nitrogen inlet. Then 11.5 g of monoethylene glycol, 11.5 g of ethylene glycol monomethyl ether, 14.2 g (0.2 mol) of N-vinylformamide and 0.281 g ($1x10^{-3}$ mol) of phenacyl morpholinedithiocarbamate were charged to the flask under nitrogen stream. The nitrogen flow was continued for 15 min. The oil bath was preheated to 60°C. 0.066 g ($0.4x10^{-3}$ mol) of AIBN was added to this mixture, nitrogen flow was continued for additional 5 min. and flask was placed in oil bath. The mixture was stirred continuously with a magnetic bar. To follow kinetics of the polymerization, samples (approx. 2 ml) were withdrawn via

pipette at appropriate time intervals, to inspect the polymerization yields. The polymer samples were isolated by precipitation in 17 - 18 ml acetone. The samples were centrifuged and solvent was decanted. Samples were washed additional two times with acetone, centrifuged and decanted. Vacuum-dried samples were weighed and percentage polymer contents of the samples were used to build up of conversion-time plot (Fig-4.2).

3.3.8. Block Copolymerization

N-vinylformamide – styrene block copolymers were prepared starting either from PNVF or PS prepolymers as described below.

3.3.8.1. Block Copolymers Starting From poly(N-vinylformamide)

Three 100 ml three-necked flasks were mounted on thermostated oil baths. The flasks were equipped with reflux condenser and nitrogen inlet. Then 1 g poly(N-vinylformamide) samples were dissolved in 20 ml of 10 % LiCl solution of NMP in each flask. 1 ml, 2 ml and 4 ml of styrene were charged respectively to each flask under nitrogen stream. 4 ml of ethylene glycol was added to the flask containing 4 ml styrene for better dissolution of poly(N-vinylformamide). The nitrogen flow was continued for 15 min. The oil baths were preheated to 60°C. 0.018 g ($0.11x10^{-3}$ mol) of AIBN was added to each mixture, nitrogen flow was continued for additional 5 min. and flasks were placed in oil baths. The mixtures were stirred continuously with magnetic bar. After approximately 96 hours reaction time the polymers were precipitated in 50 ml acetone, filtered and vacuum dried overnight at 50°C. Isolated yields were 1.1 g, 2.0 g, 1.6 g respectively for 1 ml, 2 ml and 4 ml styrene contents.

3.3.8.2. Block Copolymers Starting From Polystyrene

Three 100 ml three-necked flasks were mounted on thermostated oil baths. The flasks were equipped with reflux condenser and nitrogen inlet. Then 0.5 g polystyrene samples were dissolved in 15 ml, 18 ml and 20 ml of 10 % LiCl solution of NMP. 2 ml, 3 ml and 4 ml of styrene were charged respectively to each flask under nitrogen stream. The nitrogen flow was continued for 15 min. The oil baths were preheated to 60°C. 0.020 g of AIBN was added to each mixture, nitrogen flow was continued for additional 5 min. and flasks were placed in oil baths. The mixtures were stirred continuously with magnetic bar for 96 hours and the polymers were precipitated in

50 ml methanol, filtered and dried as described above. Isolated yields were 1.1 g, 1.2 g and 1.5 g respectively for 2 ml, 3 ml and 4 ml N-vinylformamide contents, respectively.

3.3.9. Hydrolysis of Poly(N-vinylformamide)

This homopolymer was hydrolyzed for better understanding solubility behaviors of the block copolymers.

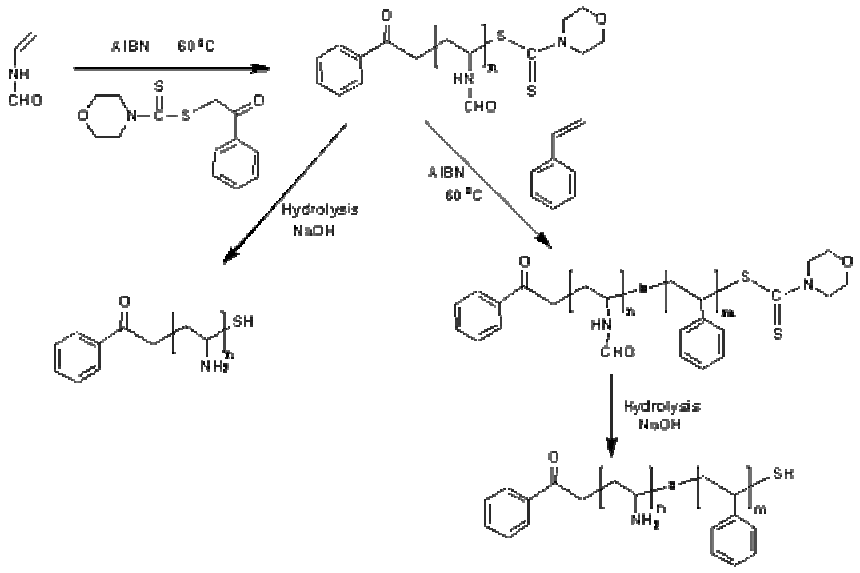
Hydrolysis of poly (N-vinylformamide) sample was carried out by 30 % NaOH solution in water. 0.5 g of polymer sample was dissolved in 3 - 4 ml hot water. Then, 5 ml of 30% sodium hydroxide solution was added and heated at 80°C for 1 hour. The mixture became clear first, and then an oily layer phase appeared while stirring. The reaction content was cooled and water was decanted. The residual polymer was dried under vacuum at 60°C for 5 hours. The yield was 0.23 g.

3.3.10. Hydrolysis of N-vinylformamide Segments of the Block Copolymers

Hydrolysis of block copolymer sample was carried out as by concentrated NaOH solution in water. In a typical procedure 0.5 g of polymer sample obtained via end group transformation was dissolved in hot water (approximately 15%). Then, 5 ml of 30% sodium hydroxide solution was added and heated at 80°C for 1 hour. The mixture became clear first, then an oily layer phase appeared while stirring. The reaction content was cooled and water was decanted. The residual polymer was dried under vacuum at 60°C for 5 hours. The isolated yield was 0.31 g.

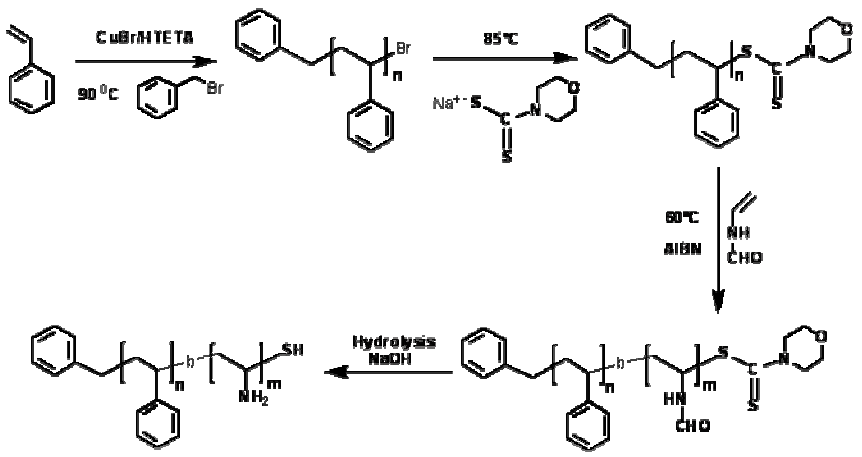
4. RESULTS and DISCUSSION

Two routes were followed for preparing vinyl amine-styrene block copolymers as depicted in Scheme 4.1 and Scheme 4.2. In the first route linear living poly(N-vinylformamide) was prepared by RAFT methodology. Then this was used as macro-transfer agent for chain extension with styrene. The resulting block copolymer, poly(N-vinylformamide)-*block*-poly(styrene) was subjected to basic hydrolysis. Hydrolysis of poly(N-vinylformamide) block gave corresponding block copolymer of vinyl amine, poly(vinylamine)-*block*-poly(styrene) (Scheme 4.1).



(4.1)

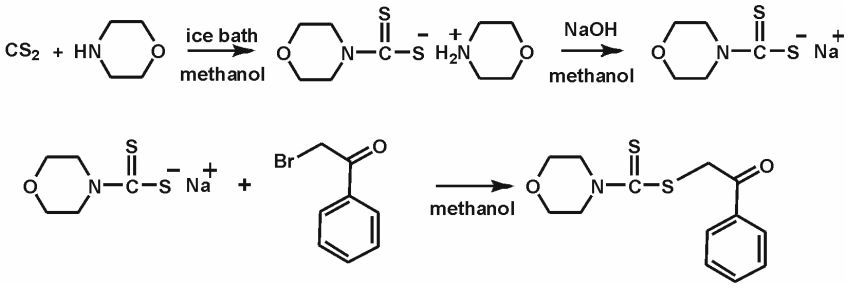
In a second approach well defined poly(styrene) block was prepared first by ATRP method. Bromoalkyl end-group of this polymer was transformed into morpholinedithiocarbamate end group by reacting with excess of sodium morpholinedithiocarbamate salt in NMP. The resulting polymer was employed as macro RAFT agent for block copolymerization with NVF (Scheme 4.2).



(4.2)

4.1. Synthesis of Homopolymers by RAFT Method

In this work, we have studied first polymerizabilities of N-vinylformamide and styrene by using phenacyl morpholinedithiocarbamate as chain transfer agent which was prepared in our laboratory by the reaction sequences shown in Scheme 4.3. The RAFT agent obtained was chosen because of two main reasons: Firstly, the phenacyl group (R group) in the structure is easy living group which fulfills requirements for efficient transfer of the radicals in the beginning of the polymerization. Secondly, morpholino group (Z group) was considered to be reasonably polar to induce sufficient activity on the C=S double bond. This property was considered to provide high control efficiency on the polymerization [127]. In addition to this, the Z group must have electron withdrawing ability to increase stability of the intermediate radical.



(4.3)

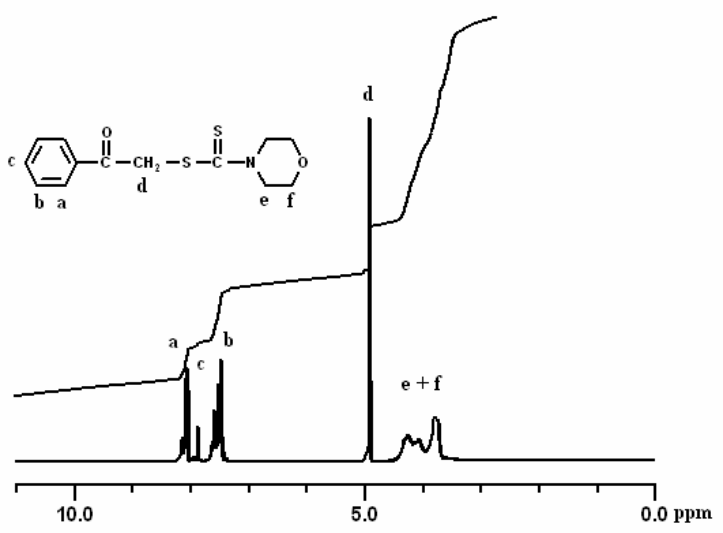


Figure 4.1 ^{1}H-NMR of the RAFT agent (phenacyl morpholinedithiocarbamate)

^{1}H-NMR spectrum of this product in Fig-4.1 establishes the proposed structure. Thus, aromatic proton signals of phenyl ring lie in 7.3 – 8.2 ppm range. The singlet appearing at 5.0 ppm is associated with the protons of methylene bridge. The protons of morpholino group appear as broad multiplet in 3.7 – 4.5 ppm range. The integral ratio of the signals clearly justifies the structure, as observed in Fig-4.1.

Kinetic studies for RAFT polymerization were followed for both of the monomers, styrene and N-vinylformamide.

The polymerization of NVF monomer showed first order kinetics with a good regression coefficient (R: 0.9943) as depicted in Fig-4.2. From the slope of the straight line the rate constant of the polymerization was found to be 4.73×10^{-3} min^{-1} which corresponds to 7.88×10^{-5} s^{-1}.

M_w measurements of PNVF were carried out by HPLC using water as solvent. M_w – conversion plot of this polymerization (Fig-4-3) is implying poor control of the chain growth in the polymerization. Increasing of the molecular weight is not linear throughout the polymerization and significantly deviates from linearity at the conversions above 75 %. The corresponding polydispersity indexes lie in 1.7 – 2.6. This reveals that morpholinedithiocarbamate end group on growing poly(N-vinylformamide) chains do not provide a good control, most probably due to high propagation rate of the polymerization in comparison to the chain transfer constant.

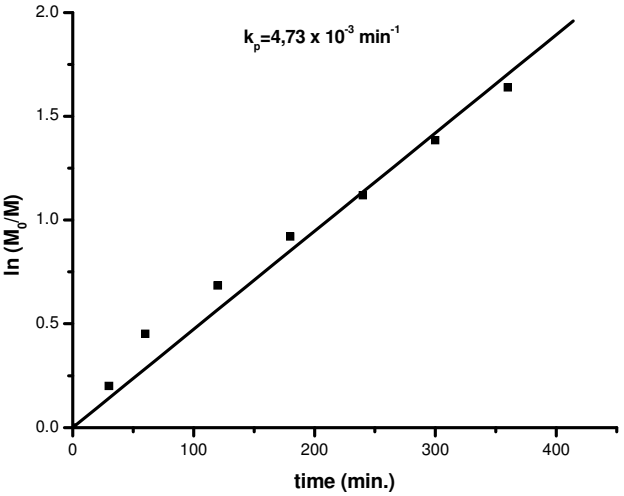


Figure 4.2 First order kinetics plot for RAFT polymerization of N-vinylformamide. (Conditions: 60°C, in ethylene glycol / ethylene glycol monomethyl ether (1:1), total monomer conc.= 37.5 %, [Monomer] / [RAFT agent] /[AIBN] : 500/2.5/1)

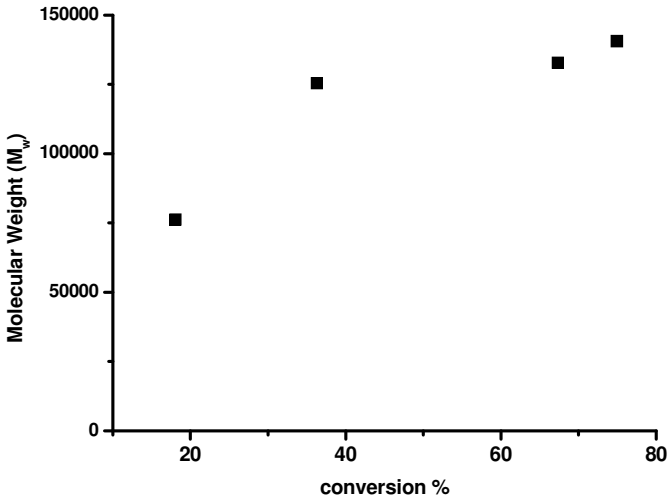


Figure 4.3 M_w – conversion plot of RAFT polymerization of N-vinylformamide. (Conditions: 60°C, in ethylene glycol / ethylene glycol monomethyl ether (1:1), total monomer conc.= 37.5 %, [Monomer] / [RAFT agent] /[AIBN] : 500/2.5/1)

Similar RAFT polymerization using phenacyl morpholinedithiocarbamate as chain transfer agent was carried out with styrene monomer at the same temperature, using 1,4-dioxane as solvent. The polymerization in this case was shown to be slow. The conversion was around 61 % after 52 h of polymerization. Kinetics of polymerization, however, indicated fairly good first order kinetics, with a good regression coefficient (R: 0.9944), as shown in Fig-4.4. From the slope of the straight

line the rate constant of the polymerization was found to be $3.24x10^{-4}$ min^{-1} which corresponds to $5.4x10^{-6}$ s^{-1}.

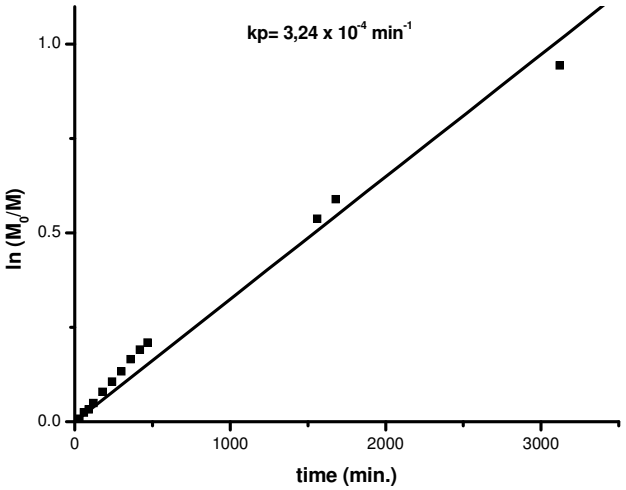


Figure 4.4. First order kinetics plot for RAFT polymerization of styrene. (Conditions: 60°C, in 1,4-dioxane, total monomer conc.= 29.7 %, [Monomer] / [RAFT agent] /[AIBN] : 250/2.5/1)

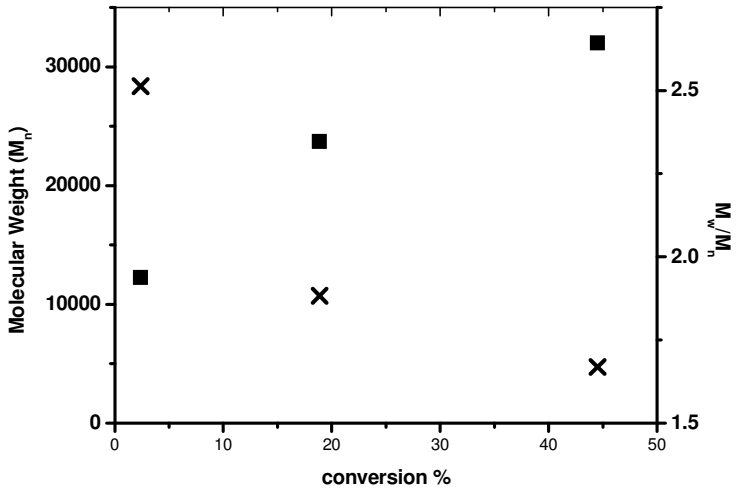
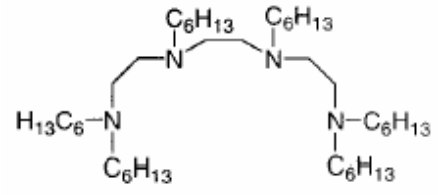


Figure 4.5 M_n versus conversion for the polymerization of styrene (■), and corresponding molecular weight distribution (M_w/M_n) versus conversion (**x**).

Number average molecular weight was seemed to be nearly proportional to the conversion. The M_n values varied from 12.200 to 32.000 within 1 – 28 h. The polydispersity was around 2.5 for the 12.000 Daltons molecular weight of polymer. For the prolonged reaction times i.e. 28 h the polydispersity falls around 1.7 and remains almost constant around this value (Fig-4.5).

4.2. Preparation of Poly(styrene) by ATRP

In order to prepare block copolymers with good polydispersities, poly(styrene) was prepared by ATRP in bulk conditions at 90°C using H-TETA as ligand [126] for CuBr. Benzyl bromide was employed as initiator. Structure of the ligand H-TETA is shown in Scheme 4.4.



(4.4)

This ligand was used due to excellent solubility of its copper complexes in various organic solvents. Number average molecular weight of the resulting polymer was determined to be 8000 by GPC and the polydispersity was 1.14. (Fig-4.6).

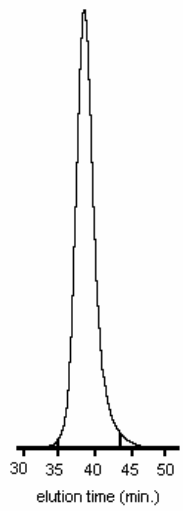


Figure 4.6 GPC chromatogram of poly(styrene) prepared by ATRP method. (Waters ultrastyragel columns (HR 5E series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min, refractive index detector, at 30°C. Molecular weights were calculated by using monodisperse poly(styrene) standards.)

4.3. Synthetic Strategy for the Block Copolymers

Synthesis of amphiphilic block copolymers is difficult task in principle. The difficulty is to find a suitable solvent capable of dissolving both blocks.

As to our knowledge, PS-PNVF block copolymers have not been described in the literature. The additional difficulty in preparing this block copolymer is that NVF

monomer is not polymerizable by ATRP technique. This monomer is polymerizable by RAFT method. However, control of chain growth is extremely terrible considering with a lowest PDI of 1.7 [7]. Most probably this is due to low radical transfer ability of the dithiocarbamate or dithioester functionalities on the dorming chain ends of its polymer. Another difficulty is appropriate choice of the best solvent for the copolymerization as stated above.

We have tested many binary solvent mixtures which are able to dissolve PS and PNVF. However, commercial solvent mixtures did not work. After many trial and errors, finally we have found that NMP containing 10% LiCl is better solvent for both of the blocks. Therefore, we have carried out the copolymerization experiments by using this solvent.

4.4. Properties of the Block Copolymers

PS-*block*-PNVF was obtained by two different approaches as stated above. In the first approach, PNVF was prepared by RAFT process, then, this was used macro-chain transfer agent for chain extension with styrene. In the second route, the copolymer was prepared by polymerization of NVF using poly(styrene) prepolymer with morpholinedithiocarbamate end group. A well defined poly(styrene) (Mn:8000, PDI: 1.14) was obtained by ATRP process and bromoalkyl end group of this polymer was transformed into morpholinedithiocarbamate group, by condensation with sodium salt of morpholinedithiocarbamic acid. The resulting PS was employed as macro-chain transfer agent to obtain PS-*block*-PNVF. Although PNVF first approach gives PNVF-*block*-PS in this report, we represent both block copolymers as PS-*block*-PNVF, due to their structural similarities.

The block copolymers prepared by starting from PS prepolymer were precipitated in methanol which is solvent for PNVF block but non-solvent for PS. The product was further purified by dissolving and reprecipitation in THF which is good solvent for PS. Therefore, the copolymer isolated can be considered as fairly pure product free of homopolymer impurities.

The block copolymers obtained by either routes were found not to be completely soluble in individual solvents for each block.

Also there is no pure solvent for dissolving the copolymers. For this reason we were not able to trace GPC of the block copolymers. Since the use of mixed solvents is not advisable for GPC measurements, the GPC traces of block copolymers are not available at this moment. This is common problem of the amphiphilic block copolymers

^{1}H-NMR spectrum (Fig-4.7) of the block copolymers were recorded in a mixture DMSO–d_6/DMF-d_7. Although, DMSO-d_6 is a good solvent for PNVF block it is not able to dissolve PS block at room temperature, and the deuterioted solutions became cloudy upon standing at room temperature.

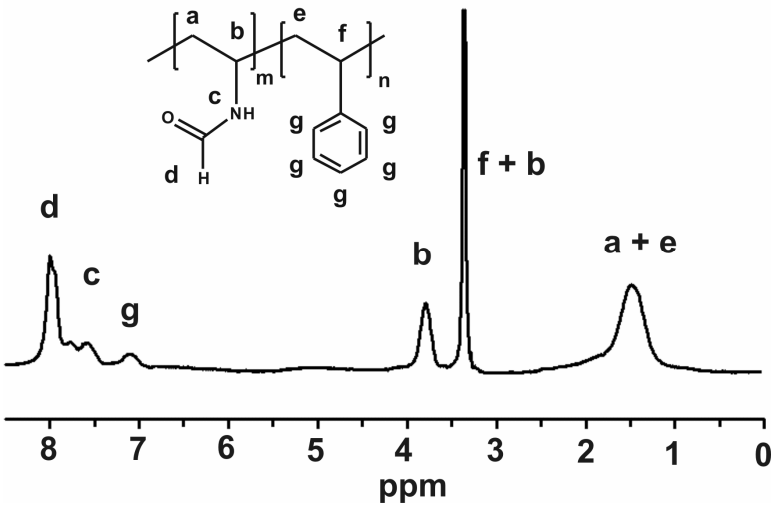


Figure 4.7 ^{1}H-NMR spectrum of block copolymer, obtained by polymerization of NVF, using PS prepolymer with morpholinedithiocarbamate end group (in DMSO-d_6/DMF-d_7).

^{1}H-NMR spectrum (Fig-4.7) is a representative example showing proton signals of PS-*block*-PNVF copolymer obtained by starting ATRP prepared PS. Interestingly, aromatic proton signals of PS block are clearly observed around 7.0 ppm as weak signals.

This result indicates formation of block copolymer. Weakness of aromatic proton signals of PS block is due to fact that even this solvent mixture is not a good solvent for this block. This is common behavior of amphiphilic block copolymers that the less soluble block protons in a selective solvent is generally invisible. Or else these may be observed as weak signals only, as in the present case.

Unfortunately we were not able to estimate ratio of the block lengths of the block copolymers based on ^{1}H-NMR spectra in DMF-d_7-DMSO-d_6 mixture.

To observe proton signals of the both blocks we have used trichloroacetic acid as solvent. Fortunately, the proton signals associated with both of the blocks were observable in this solvent (Fig-4.8). In this spectrum, integral ratio of formamido group proton of PNVF block to that of aromatic protons is approxiamately 1/6. From this, molar ratio of the block lengths PS/PNVF was estimated as 1.2/1.Therefore, repeating units of PNVF block should be 8000 / (104x1.2) = 64.1. This corresponds to 4550 Daltons of molecular weight for the PNVF block. The resulting copolymer can be represented simply as, $(PS)_{77}$-*block*-$(PNVF)_{64}$.

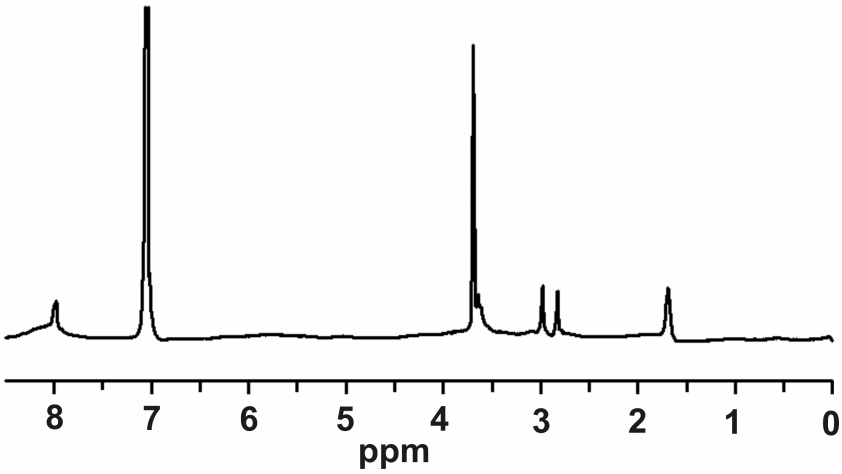


Figure 4.8. ^{1}H-NMR spectrum of block copolymer, obtained by polymerization of NVF, using PS prepolymer with morpholinedithiocarbamate end group (in trichloro acetic acid).

FTIR spectra in Fig-4.9 show that the copolymer exhibits typical IR spectrum of styrene and N-vinylformamide polymers. Thus, C=O stretching vibration band and N-H plain bending vibration bands in IR spectrum of PNVF are observed at 1680 and 1620 cm^{-1}. These typical peaks involved in the spectrum of the block copolymer shown at the bottom. The latter one seems to be combined with skeletal ring vibration of the PS block. These results can be considered as evidence for the formation of block copolymers.

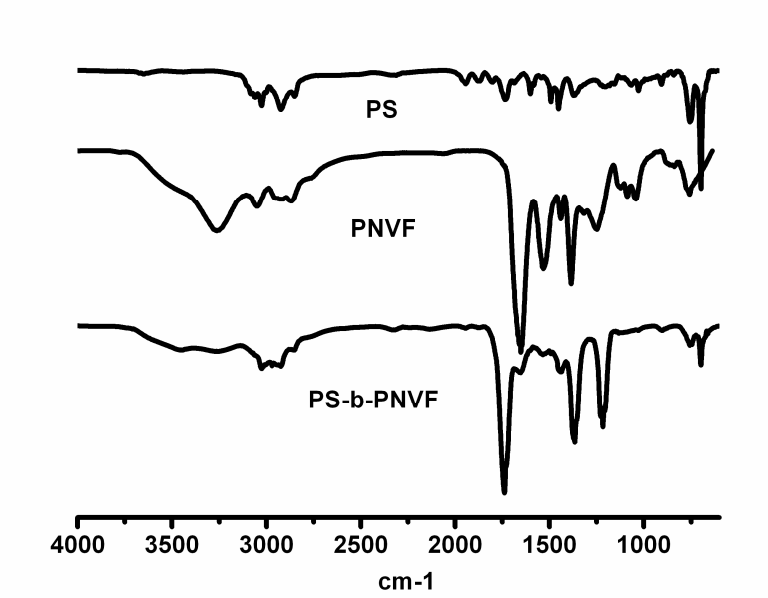


Figure 4.9 FTIR spectra of homopolymers PNVF, PS and block copolymer PS-*block*-PNVF

4.5. Hydrolysis of PNVF and Block Copolymers

To attain vinyl amine block copolymers the copolymers prepared were subjected to hydrolysis using sodium hydroxide solution. Before that PNVF homopolymer was hydrolyzed to investigate the hydrolysis conditions.

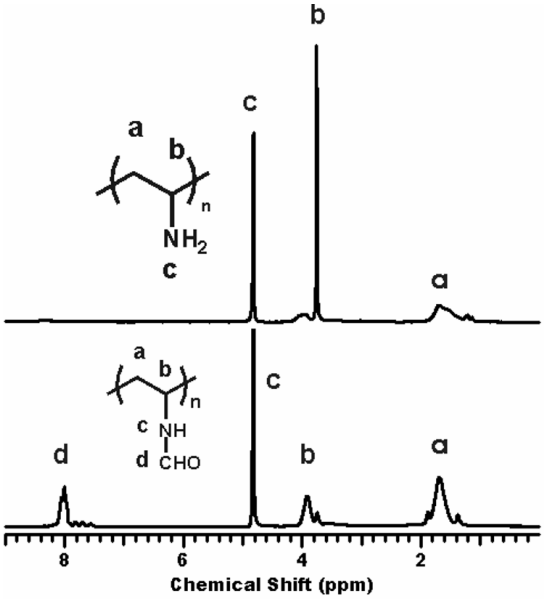


Figure 4.10 ^{1}H-NMR spectra of PNVF and its hydrolysis product in D_2O

Fig-4.10 shows that positions of the aliphatic proton signals do not undergo any significant shift and their locations do not change practically, after hydrolysis. The

peak associated with formamido group proton at 8.0 ppm disappears as expected. NH_2 protons of poly(vinylamine) is observed around 4.5 ppm. However, this peak was absent in D_2O solvent due to their exchange with deuterium.

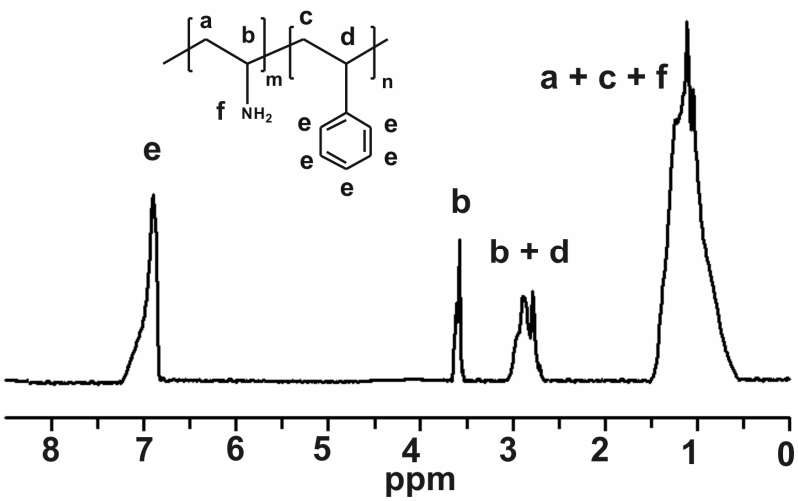


Figure 4.11 ^{1}H-NMR spectrum of hydrolysis product of block copolymer, obtained by polymerization of styrene, using PNVF prepolymer (in DMSO-d_6).

Similar differences are observed in ^{1}H-NMR spectrum of hydrolysis product of block copolymer (Fig-4.11). The protons of carbon atoms linked to amino group give rise to two signals at 2.8 and 3.6 ppm.

Most significant change in this spectrum is that, formamido proton signals of PNVF block around 8.0 ppm dissappear almost completely.

However, invisible aromatic protons of PS block gives rise a broad signal at 6.9 ppm. Since the intensity of the former (in Fig-4.7) was weak, this is a good evidence for presence of PS block in the copolymer.

The aliphatic proton signals of poly(vinylamine) block undergoes upfield shift and appear as a broad signal in 0.6 – 1.4 ppm range.

Since increment of molecular weight by chain extension could not be verified by GPC, in order to show any rise in molecular weight we have decided to compare intrinsic viscosities of the precursor polymer with those of the block copolymers. Viscosity measurements of polymers and block copolymers were performed in 1:1 DMF:DMSO mixture by capillary viscosimetry technique using Ubbelohde viscometer at 25°C. The results are tabulated in Table 4.1.

Table 4.1 Viscosity records for PS and PS-*block*-PNVF

Polymer	**Molecular weight**[a]	**[η]**[b]
Poly(styrene)	8000	0.108
PS-*block*-PNVF[c]	—	0.177
PS-*block*-PNVF[d]	—	0.170

[a] M_n determined by GPC
[b] In 1:1 DMF:DMSO mixture, at 25°C
[c] Block copolymer synthesized starting from 0.5 g poly(styrene) and chain extension with 2 ml NVF
[d] Block copolymer synthesized starting from 0.5 g poly(styrene) and chain extension with 3 ml NVF

The viscosities in the table are in accordance with increasing chain length of the PNVF block. While the intrinsic viscosity of poly(styrene) prepared by ATRP method was 0.108, those of two block copolymers prepared by the chain extension with NVF was found to be as 0.177 and 0.170. The increase in intrinsic viscosity implies molecular weight increment after chain extensions. Therefore, overall results indicate formation of block copolymer structures.

CONCLUSION

Despite non-existence of common organic solvent dissolving PNVF and PS, we were able to synthesize their block copolymers. It was found that, the solvent, NMP with 10% LiCl was appropriate for dissolution of either block. The block copolymers were prepared either by sequential RAFT polymerization of the two monomers starting from NVF or end group transformation of ATRP-growth PS and following chain extension with NVF monomer by RAFT methodology.

PNVF block of the resulting copolymer was hydrolyzed to give poly (vinyl amine)-*block*-poly (styrene). It is not doubt that this amphiphilic copolymer with poly (vinyl amine) reactive block is very useful and will find numerous applications to develop new materials.

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